

**The crystal structures of diaquatetra( $\beta$ -picoline)M(II) perchlorate,  
[M(H<sub>2</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Cu, Co)**

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Crystals of the Cu(II), Co(II), and Ni(II)  $\beta$ -picoline complexes ([M(H<sub>2</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, M = Cu, Co, Ni) all showed monoclinic rhombohedral morphology and were shown by diffraction methods to be isomorphous. The structures of the Cu(II) and Co(II) complexes have been determined in detail.

Atom	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (deg)	<i>D<sub>m</sub></i>	<i>D<sub>s</sub></i>	Colour
Cu(II)	15.292(4)	9.672(2)	20.579(5)	94.73(2)	1.45(1)	1.467	Blue
Co(II)	15.878(12)	9.374(3)	20.661(7)	96.50(4)	1.45(1)	1.448	Pink
Ni(II)	15.7	9.3	20.4	96.5	1.44(1)		Pale blue

The space group of crystals of the three complexes is *C2/c*. The structures were solved by the Patterson method. The structures of the Cu(II) and Co(II) complex were refined to a final *R<sub>w</sub>* (on  $|F|$ ) of 0.050 and 0.068 for 1918 and 2455 independent reflections, respectively, as measured with a modified Picker diffractometer. The structure of these complexes consists of coordination polyhedra with formulation [M(H<sub>2</sub>O)<sub>2</sub>( $\beta$ -picoline)<sub>4</sub>]<sup>2+</sup> and perchlorate counterions. The ions are connected by hydrogen bonds of average length 2.76 Å in the Co(II) complex and 2.82 Å in the Cu(II) complex. The four N atoms of the  $\beta$ -picoline ligands form an equatorial plane with average [M—N] distances of 2.17 Å in the Co(II) complex and 2.03 Å in the Cu(II) complex. The water ligands are in apical positions with [M—O] distances of 2.124(6) Å and 2.493(10) Å in the Co(II) and Cu(II) complexes respectively. This large difference in bond lengths is manifested in marked differences in the appearance of crystals of the two compounds and is consistent with an expected Jahn–Teller effect. The thermal factors suggest that the perchlorate ion undergoes enhanced librational motion.

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Les cristaux des complexes ([M(H<sub>2</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, M = Cu, Co, Ni) ont tous une forme rhomboédrique monoclinique et les méthodes de diffraction révèlent qu'ils sont isomorphes. On a déterminé en détail les structures des complexes du Cu(II) et de Co(II).

Atomie	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$ (deg)	<i>D<sub>m</sub></i>	<i>D<sub>s</sub></i>	Couleur
Cu(II)	15.292(4)	9.672(2)	20.579(5)	94.73(2)	1.45(1)	1.467	Bleu
Co(II)	15.878(12)	9.374(3)	20.661(7)	96.50(4)	1.45(1)	1.448	Rose
Ni(II)	15.7	9.3	20.4	96.5	1.44(1)		Bleu pale

Les cristaux des trois complexes appartiennent au groupe d'espace *C2/c*. On a résolu les structures par la méthode de Patterson et on a ajusté celles du Cu(II) et du Co(II) jusqu'à des valeurs conventionnelles de *R<sub>w</sub>* (sur *F*) de 0.050 et 0.068 pour respectivement 1918 et 2455 réflexions indépendantes à l'aide d'un diffractomètre de Picker modifié. La structure de ces complexes consiste en une coordination polyédrique de formule [M(H<sub>2</sub>O)<sub>2</sub>( $\beta$ -picoline)<sub>4</sub>]<sup>2+</sup> et des ions opposés de perchlorate. Les ions sont reliés par des liaisons hydrogène de longueur moyenne de 2,76 Å dans le complexe de Co(II) et de 2,82 Å dans le complexe de Cu(II). Les quatre atomes d'azote des ligands  $\beta$ -picoline forment un plan équatorial avec des distances moyennes [M—N] de 2,17 Å dans le complexe de Co(II) et de 2,03 Å dans le complexe du Cu(II). Les ligands eau sont disposés au sommet avec des distances [M—O] de 2,124(6) Å et de 2,493(10) Å dans les complexes de Co(II) et de Cu(II) respectivement. Cette grande différence au niveau des longueurs de liaison se manifeste dans les différences profondes d'apparence des cristaux des deux composés et elle est en accord avec l'effet de Jahn–Teller attendu. Les facteurs thermiques suggèrent que l'ion perchlorate subit un mouvement de libration accru.

[Traduit par le journal]

### Introduction

This research is part of a project to form a variety of mixed valence binuclear transition metal compounds by reacting anhydrous complexes with superoxides as has been done with DMSO (1). However, analyses of our products of the synthesis claimed by Brown *et al.* (2) to produce the anhydrous complexes were puzzling. Each of these complexes was found to consist of perchlorate ions and a metal atom coordination polyhedron with four  $\beta$ -picoline and two water ligands by X-ray crystal structure studies. These complexes imply that  $\beta$ -picoline does not substitute readily for all six water molecules in  $M(\text{H}_2\text{O})_6(\text{ClO}_4)_2$  as does DMSO.

### Experimental

#### Preparation of the compounds

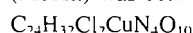
$[\text{Cu}(\text{H}_2\text{O})_2(\beta\text{-pic})_4](\text{ClO}_4)_2$  (blue),  $[\text{Co}(\text{H}_2\text{O})_2(\beta\text{-pic})_4](\text{ClO}_4)_2$  (pink), and  $[\text{Ni}(\text{H}_2\text{O})_2(\beta\text{-pic})_4](\text{ClO}_4)_2$  (pale blue) were prepared by dissolving the appropriate hydrated metal perchlorate in a minimum of 1:1 diethyl ether:95% ethanol, the picoline complexes being formed

by dropwise addition of a slight excess of the appropriate picoline, with stirring. All complexes precipitated on refrigeration at 0°C and were recrystallized twice from acetone, dried 14 h at 80°C under high vacuum, and stored in sealed bottles over indicating Drierite, in a desiccator.

Analyses of the  $\beta$ -picoline complexes suggested the general formula  $M(\beta\text{-pic})_4(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ . In addition, Karl Fisher titrations were carried out to measure the quantities of water present in all samples. Infrared spectra also revealed distinct bands in the region of 3400  $\text{cm}^{-1}$  for all complexes, indicating the presence of water. However, it could not be rationalized as strictly complexed water, as in no case did the mole ratio of metal to unknown (assuming the unknown moiety to be water) take integral values.

#### X-ray crystallographic analysis

Precession photographs provided space groups and approximate unit cell dimensions. Accurate lattice parameters of the Cu(II) and Co(II) complexes were obtained by a least-squares treatment of the diffractometer setting angles for ca. 20 reflections for which  $2\theta_{hkl}$  ( $\text{MoK}\alpha$ ) was between 40 and 45°. Crystal data at 18(2)°C are:



$$fw = 670.3$$

TABLE 1. Fractional coordinates for  $[\text{M}(\text{H}_2\text{O})_2(\beta\text{-pic})_4](\text{ClO}_4)_2$  ( $M = \text{Cu}, \text{Co}$ ) with estimated standard deviations in parentheses and isotropic thermal parameters,  $U (\times 10^3) (\text{\AA})$

Atom	x		y		z		$U_{\text{eq}}/U_{\text{iso}}^*$	
	M = Cu	M = Co	M = Cu	M = Co	M = Cu	M = Co	M = Cu	M = Co
M	0.5000	0.5000	0.09707(15)	0.10262(9)	0.2500	0.2500	49	46
C1	0.0879(2)	0.0832(1)	0.0989(3)	0.1010(2)	0.3870(1)	0.3790(1)	79	66
O(1)	0.1574(5)	0.1564(4)	0.1499(10)	0.1624(9)	0.4175(5)	0.4057(4)	254	237
O(2)	0.1076(7)	0.1036(4)	0.0228(10)	0.0066(6)	0.3361(4)	0.3317(3)	250	173
O(3)	0.0452(7)	0.0388(6)	0.2142(11)	0.2152(9)	0.3714(4)	0.3603(4)	265	260
O(4)	0.0461(7)	0.0496(6)	0.0262(9)	0.0342(6)	0.4270(5)	0.4268(3)	259	208
O(5)	0.5000	0.5000	-0.1584(9)	-0.1239(6)	0.2500	0.2500	69	67
O(6)	0.5000	0.5000	0.3571(12)	0.3295(6)	0.2500	0.2500	111	80
N(1)	0.3699(3)	0.3654(2)	0.1064(6)	0.1134(4)	0.2192(3)	0.2165(2)	55	51
C(1)	0.3340(4)	0.3283(3)	0.0228(8)	0.0320(5)	0.1727(3)	0.1680(2)	51	50
C(2)	0.2450(5)	0.2415(3)	0.0234(8)	0.0270(5)	0.1520(4)	0.1494(2)	58	57
C(3)	0.1952(6)	0.1927(4)	0.1157(11)	0.1121(8)	0.1846(5)	0.1858(3)	82	76
C(4)	0.2295(6)	0.2296(4)	0.2023(10)	0.1979(7)	0.2332(5)	0.2347(3)	86	78
C(5)	0.3184(5)	0.3152(4)	0.1951(9)	0.1966(6)	0.2486(4)	0.2480(3)	71	66
N(2)	0.4700(3)	0.4707(2)	0.0941(7)	0.0956(4)	0.3435(3)	0.3500(2)	56	51
C(6)	0.4141(5)	0.4125(3)	0.0005(9)	0.0038(5)	0.3650(4)	0.3691(2)	57	56
C(7)	0.3856(5)	0.3834(3)	-0.0004(9)	0.0045(6)	0.4271(4)	0.4288(2)	61	61
C(8)	0.4157(6)	0.4165(4)	0.1031(11)	0.1086(7)	0.4685(4)	0.4726(3)	70	69
C(9)	0.4731(6)	0.4756(4)	0.1996(10)	0.2025(6)	0.4476(5)	0.4546(3)	74	69
C(10)	0.4988(5)	0.5025(3)	0.1915(8)	0.1933(5)	0.3858(4)	0.3941(2)	55	54
C(11)(C(7))	0.3249(5)	0.3185(5)	-0.1127(9)	-0.1042(11)	0.4484(4)	0.4450(4)	91	90
C(12)(C(2))	0.2080(4)	0.2045(6)	-0.0689(9)	-0.0665(10)	0.1001(4)	0.0958(4)	91	89
H(1)(C(1))	0.370(2)	0.360(2)	-0.041(4)	-0.024(4)	0.152(2)	0.145(2)	0(12)	32(11)
H(3)(C(3))	0.141(4)	0.145(3)	0.112(7)	0.123(6)	0.176(3)	0.176(2)	69(24)	74(19)
H(4)(C(4))	0.187(4)	0.198(3)	0.268(8)	0.269(5)	0.260(3)	0.266(2)	119(30)	81(16)
H(5)(C(5))	0.342(4)	0.341(3)	0.259(7)	0.249(5)	0.286(3)	0.284(2)	116(31)	68(16)
H(6)(C(6))	0.397(3)	0.390(2)	-0.077(5)	-0.063(4)	0.338(2)	0.331(2)	32(16)	49(12)
H(8)(C(8))	0.395(3)	0.401(3)	0.104(7)	0.111(5)	0.516(3)	0.514(2)	83(23)	78(17)
H(9)(C(9))	0.492(4)	0.496(3)	0.264(5)	0.262(4)	0.476(2)	0.483(2)	46(21)	50(14)
H(10)(C(10))	0.528(3)	0.548(2)	0.255(4)	0.256(4)	0.369(2)	0.382(2)	0(14)	33(11)
H(11)(C(11))	0.294(6)	0.313(3)	-0.101(10)	-0.099(6)	0.476(5)	0.482(3)	230(43)	74(21)
H(12)(C(11))	0.348(5)	0.335(6)	-0.207(8)	-0.203(10)	0.439(4)	0.441(4)	150(30)	196(46)
H(13)(C(11))	0.269(5)	0.264(6)	-0.126(8)	-0.129(10)	0.417(4)	0.406(5)	149(31)	217(42)
H(14)(C(12))	0.241(4)	0.243(4)	-0.126(7)	-0.128(6)	0.079(3)	0.077(3)	121(27)	107(26)
H(15)(C(12))	0.194(4)	0.198(6)	-0.023(8)	-0.023(9)	0.059(3)	0.052(4)	137(29)	184(41)
H(16)(C(12))	0.158(4)	0.154(5)	-0.107(7)	-0.073(8)	0.106(3)	0.092(4)	108(23)	128(33)
H(17)(O(6))	0.491(5)	0.465(3)	0.384(8)	0.370(5)	0.219(3)	0.228(3)	74(31)	85(21)
H(18)(O(5))	0.472(5)	0.485(4)	-0.207(7)	-0.170(6)	0.223(3)	0.220(2)	89(30)	89(21)

$$*U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

TABLE 2. Interatomic distances (Å), angles (deg), and mean plane data for  $[M(H_2O)_2(\beta\text{-pic})_4](ClO_4)_2$  ( $M = Cu, Co$ ), with estimated standard deviations in parentheses

Bond	Distance		Bonds	Angle			
	M = Cu	M = Co		M = Cu	M = Co		
(a) Coordination spheres							
M—N(1)	2.040(5)	2.173(4)	O(5)—M—O(6)	180	180		
M—N(2)	2.015(5)	2.170(4)	N(1)—M—N(2)	90.3(2)	89.7(1)		
M—O(5)	2.470(9)	2.123(5)	N(1)—M—O(5)	92.5(2)	92.7(1)		
M—O(6)	2.515(12)	2.126(6)	N(2)—M—O(5)	89.2(2)	88.3(1)		
(b) Picolanyl groups							
N(1)—C(1)	1.336(9)	1.341(6)	C(1)—N(1)—C(5)	119.2(6)	117.4(4)		
N(1)—C(5)	1.342(10)	1.336(7)	C(6)—N(2)—C(10)	116.6(6)	116.8(4)		
N(2)—C(6)	1.344(10)	1.355(7)	C(1)—C(2)—C(12)	121.8(7)	121.6(5)		
N(2)—C(10)	1.333(10)	1.349(6)	C(3)—C(2)—C(12)	123.4(7)	123.1(6)		
Mean C—C	1.377(10)	1.375(8)	C(6)—C(7)—C(11)	121.1(7)	120.4(5)		
Mean CH <sub>3</sub> —C	1.495(11)	1.498(11)	C(8)—C(7)—C(11)	121.8(8)	123.0(6)		
(c) Perchlorate ion*							
	(i)	(ii)	(i)	(ii)			
Cl—O(1)	1.287(9)	1.472	1.358(7)	1.498	O(1)—Cl—O(2)	111.3(6)	107.4(4)
Cl—O(2)	1.335(10)	1.498	1.384(6)	1.530	O(1)—Cl—O(3)	99.6(6)	100.4(5)
Cl—O(3)	1.318(11)	1.544	1.314(9)	1.497	O(1)—Cl—O(4)	109.2(6)	107.1(5)
Cl—O(4)	1.291(10)	1.563	1.332(7)	1.557	O(2)—Cl—O(3)	114.6(6)	118.3(4)
Mean:	1.308(10)	1.519	1.347(7)	1.521	O(2)—Cl—O(4)	110.9(6)	111.6(4)
					O(3)—Cl—O(4)	110.8(7)	110.8(5)
					Mean:	109.4(6)	109.3(5)
(d) Hydrogen bonds							
O(5)—H(18)	0.82(7)		0.78(5)		M—O(5)—H(18)	125(5)	124(4)
O(6)—H(17)	0.70(7)		0.78(5)		M—O(6)—H(17)	112(6)	120(4)
O(5)···O(3)	2.819(10)		2.746(8)				
O(6)···O(2)	2.819(11)		2.772(7)				

\* (i) Uncorrected, (ii) corrected, TLS.

## (e) Mean plane equations

<i>Cu (II) complex:</i>	
(i) Plane through atoms N(1), C(1), C(2), C(3), C(4), C(5)	Plane equation: $-3.2143X - 6.7349Y + 14.4189Z = 1.2547$
	Displacements (Å × 10 <sup>3</sup> ): N(1)−1, C(1)8, C(2)−8, C(3)0, C(4)7, C(5)−8, C(12)−16
(ii) Plane through atoms N(2), C(6), C(7), C(8), C(9), C(10)	Plane equation: $11.4380X - 5.6029Y + 5.3600Z = 6.6935$
	Displacements (Å × 10 <sup>3</sup> ): N(2)−4, C(6)−4, C(7)8, C(8)−6, C(9)−2, C(10)7, C(11)59
<i>Co (II) complex:</i>	
(i) Plane through atoms N(1), C(1), C(2), C(3), C(4), C(5)	Plane equation: $-2.3932X - 6.9547Y + 13.7664Z = 1.3049$
	Displacements (Å × 10 <sup>3</sup> ): N(1)13, C(1)0, C(2)−13, C(3)13, C(4)0, C(5)−13, C(12)−19
(ii) Plane through atoms N(2), C(6), C(7), C(8), C(9), C(10)	Plane equation: $11.0207X - 5.9072Y + 5.5302Z = 6.5652$
	Displacements (Å × 10 <sup>3</sup> ): N(2)−7, C(6)−14, C(7)6, C(8)−25, C(9)−6, C(10)11, C(11)21

Monoclinic,  $a = 15.292(4)$ ,  $b = 9.672(2)$ ,  $c = 20.579(5)$  Å,  $\beta = 94.73(2)^\circ$ ,  $V = 3033.4$  Å<sup>3</sup>,  $\rho_o = 1.46(1)$  g cm<sup>−3</sup>,  $Z = 4$ ,  $\rho_c = 1.467$  g cm<sup>−3</sup>,  $F(000) = 1388$ ,  $\mu(\text{MoK}\alpha) = 9.85$  cm<sup>−1</sup>. Absent reflections  $hkl$ ,  $h + k \neq 2n$ ;  $h0l$ ,  $l \neq 2n$ , consistent with the space groups  $C_{2h}^0-C2/c$  and  $Cs^4-Cc$ .

$C_{24}H_{32}Cl_2CoN_4O_{10}$  fw = 665.7  
 Monoclinic,  $a = 15.878(12)$ ,  $b = 9.374(3)$ ,  $c = 20.661(7)$  Å,  $\beta = 96.50(4)^\circ$ ,  $V = 3055.4$  Å<sup>3</sup>,  $\rho_o = 1.45(1)$  g cm<sup>−3</sup>,  $Z = 4$ ,  $\rho_c = 1.448$  g cm<sup>−3</sup>,  $F(000) = 1380$ ,  $\mu(\text{MoK}\alpha) = 8.19$  cm<sup>−1</sup>. The absent reflections are the same as for the Cu(II) complex.

$C_{24}H_{32}Cl_2NiN_4O_{10}$   
 Monoclinic,  $a = 15.7$ ,  $b = 9.3$ ,  $c = 20.4$  Å,  $\beta = 96.5^\circ$ ,  $\rho_o = 1.44(1)$

g cm<sup>−3</sup>. The absent reflections are the same as for the preceding two.

The intensity data of the crystals of the Cu(II) and Co(II) complexes were collected with a modified Picker diffractometer using graphite monochromated MoK $\alpha$  radiation within the limits  $3 < 2\theta < 55^\circ$  and  $3 < 2\theta < 50^\circ$  respectively for the Cu(II) and Co(II) complexes. The crystal of the Co(II) complex turned opaque gradually during data collection and the intensities of three standard reflections, monitored every 50 reflections, decreased by approximately 12%. The intensities of the standard reflections for the Cu(II) complex revealed no systematic trends during data collection. Data were corrected for the Lorentz and polarizations effects and scaled according to the changes in the standard reflections. Absorption was not considered to be important

because of the relatively small linear absorption coefficient and the small size of the crystals of both samples. The extinction condition ( $hkl$ ,  $h + k = 2n$ ;  $h0l$ ,  $l = n$ ) indicates the space group  $Cc$  or  $C2/c$ . The distribution of  $E$  values supports the latter. The structure of the Cu(II) complex was then solved by Patterson and heavy-atom methods in the space group  $C2/c$ . The structure of the Co(II) complex was assumed to be similar to that of the Cu(II) complex, as was verified by successful subsequent refinement. Of the 3508 and 2682 measured reflections for the Cu(II) and Co(II) complexes, 1918 and 2455 reflections with  $|F_o| > 3\sigma(|F_o|)$  were used in the final refinement of the structure parameters respectively. In the Cu(II) complex the refinement converged to a conventional  $R$  factor of 0.099 and  $R_w = [\sum w||F_o| - |F_c||^2 / \sum w F_o^2]^{1/2} = 0.050$  with weighting factor  $\sigma^{-2}(F_o)$ , where  $\sigma(F_o)$  is based on the counting statistics associated with the measurement of  $|F_o|$  and an additional factor derived from the excess scatter in the standard reflections over that expected from counting statistics. In the final cycle of refinement the parameter shifts were less than 0.30 of the estimated standard deviations of the parameters for all atoms.

After completion of the initial refinement of the Co(II) structure, it was observed that the structure factors for the reflections 202 and 204 as measured by the diffractometer were in poor agreement with the calculated values of the structure factors. The diffractometer values were also inconsistent with approximate values obtained from film data. Therefore, it was assumed that an error had occurred during data collection, perhaps because of an attenuator malfunction, and the film data with appropriate weights were used to replace the diffractometer data for those reflections. Weighted full-matrix least-squares refinement with anisotropic temperature factors for all atoms except hydrogen yielded an  $R$  of 0.076 and  $R_w = 0.068$ . In the final cycle of refinement the parameter shifts were less than 0.20 of the estimated standard deviations of the parameters for the non-hydrogen atoms.

The data were collected using the National Research Council of Canada diffractometer control package, using the line profiling method. The preliminary solution of the structure was also obtained with this system of programs. Subsequent calculations were carried out using Xray 76 (3).

The atomic coordinates and their standard deviations for the Cu(II) and Co(II) complexes are given in Table 1. Bond distances and angles are reported in Table 2. The atoms are labelled in Fig. 1. A view of the Cu(II) complex is given in Fig. 2. Lists of calculated and observed structure factors and thermal parameters have been placed in the Depository of Unpublished Data.<sup>1</sup>

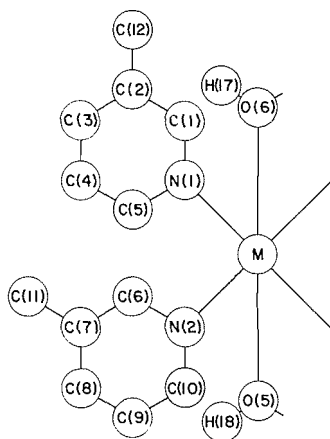


FIG. 1. Atom labelling sequence for the  $[M(H_2O)_2(\beta\text{-picoline})_4]^{2+}$  ion.

<sup>1</sup>A complete set of tabular data is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

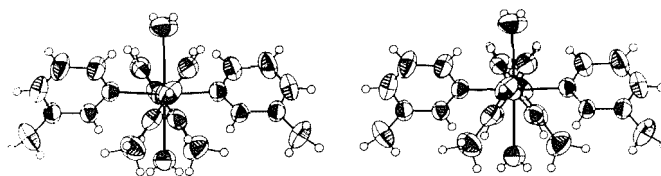


FIG. 2. View of the Cu(II) complex structure; 50% thermal ellipsoids are shown for the non-hydrogen atoms.

## Discussion

In attempts to prepare the anhydrous complexes by the reaction of Cu(II), Co(II), and Ni(II) perchlorate with  $\beta$ -picoline, no products with consistent water content analyses were obtained. Consequently, the presently reported study was undertaken to determine the water composition and the coordination about the metal ion.

Both of the structures which we examined in detail show six-coordination about the cation in the form of an approximate octahedron in the case of the Co(II) complex and in the form of an octahedron with a strong tetragonal distortion in the case of the Cu(II) complex. Each coordination site has the symmetry 2. The geometry of the latter is similar to that of the Cu(II) ion in  $Cu(NH_3)_4SO_4 \cdot H_2O$  (4), where the water molecule joins adjacent cations to form infinite chains. In the structure of  $[Cu(H_2O)_2(\beta\text{-pic})_4](ClO_4)_2$  the water molecules are hydrogen bonded to the perchlorate counterions.

The average length of the hydrogen bonds is 2.82 Å for the Cu(II) and 2.76 Å for the Co(II) complex. The four N atoms of the  $\beta$ -picoline ligands form an equatorial plane with  $[M-N]$  distances of 2.040(5) and 2.015(5) Å for the Cu(II) and 2.173(4) and 2.170(4) Å for the Co(II) complex. The former value is close to the sum of the covalent radii of Cu and N atoms and the latter is slightly longer than the sum of Co and N atoms (5). Conversely the average  $[Co-O]$  distance of 2.124(6) Å is close to that of a normal covalent bond whereas the average  $[Cu-O]$  distance of 2.493(10) Å is longer than the sum of covalent radii (5). It is of interest to note that the  $[CuN_4O_2]$  chromophore provides strong corroboration of the Jahn-Teller predictions of elongation along the axial direction.

The perchlorate counterion undergoes enhanced librational motion in spite of the fact that it is hydrogen bonded to the water molecules. Bond length corrections for thermal motion using the procedure of Shomaker and Trueblood (6) lead to increases in bond length of ca. 0.2 Å. The corrected values are larger than expected for thermally corrected perchlorate bond lengths: 1.47 Å (7). They probably are a result of the inaccuracies in bond length corrections in cases of very large amplitude thermal motion.

The  $\beta$ -picoline ligands tilt from the basal plane of the nitrogen atoms by 40–44°. All the torsion angles as well as the other important parameters of the geometry are summarized in Table 3. The packing diagram of the Cu(II) complex is shown in Fig. 3. The two water molecules coordinated to the metal ions do not account for all of the water indicated to be present by the original quantitative analysis, particularly for the Cu(II) compound. The quantitative analysis of the products of this synthesis have shown variable and usually greater water content than that implied by this structural analysis. More than one product may have been produced in the synthesis. The materials produced showed variable degrees of crystallinity and it has not been possible to verify this hypothesis by crystallographic examination.

TABLE 3. Some important mean parameters of the geometry of the complexes

Parameter	Value	
	M = Cu	M = Co
[M—N] (Å)	2.027(5)	2.171(4)
[M—O] (Å)	2.493(10)	2.124(6)
$ \langle(L-M-L) - 90^\circ $ (L = O, N) (deg)	1.1	1.5
$\tau(O-M-N-C)$ (deg)	40	44
[Cl—O] (uncorrected) (Å)	1.31(1)	1.35(1)
[Cl—O] (corrected) (Å)	1.52(3)	1.52(2)
[O—H···O] (Å)	2.82(1)	2.76(1)
$ \langle(O-Cl-O) - 109.47 $ (deg)	3.4	4.2

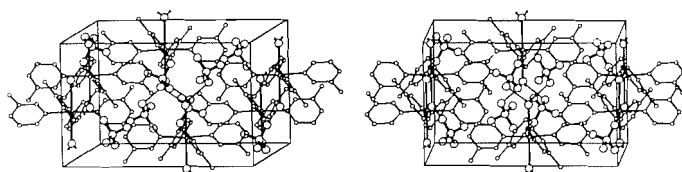


FIG. 3. Packing diagram of the Cu(II) complex. The hydrogen atoms except those associated with water are not shown for clarity.

The final difference map of the Cu(II) compound showed a negative peak corresponding to approximately  $1.5 \text{ e } \text{Å}^{-3}$  at the location of the Cu(II) ion, and four smaller peaks in the vicinity corresponding to approximately  $0.3 \text{ e } \text{Å}^{-3}$ . These peaks may arise from the fact that the weights used in the least squares calculation were not constant which would be necessary in order that the difference Fourier map would give the same results as the least squares. The weighting scheme used gave greater significance to the low angle reflections, which reflect the outer electron density better than the higher angle reflections. The presence of a substantial Jahn–Teller distortion may have perturbed the outer electron density such that the temperature factor of the Cu(II) ion as determined by least squares

was lowered from that consistent with the difference Fourier map.

The validity of this hypothesis was investigated by altering the weighting scheme to lessen the significance of the low angle reflections. The changes in the temperature factor of the Cu(II) ion were consistent with the hypothesis but the standard deviations in the atom positions were increased. The difference electron density in the vicinity of the Cu(II) ion did not become completely flat which suggests that it cannot be accurately described by any generalized ellipsoid.

The crystal structure of the Ni(II) complex is isostructural with that of the Cu(II) and Co(II) complexes. The polyhedron around the nickel atom should be much closer to that of the Co(II) complex because of the  $d^8$  configuration of Ni(II) as well as the similarity in lattice parameters between crystals of these two compounds.

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