Department of Physics, University of Texas at Arlington[1]) *(a) and*
Indian Association for the Cultivation of Science, Calcutta[2]) *(b)*

EPR and Magnetic Studies
on γ:bis(N-Methyl Salicylaldimine) Copper(II)

By

D. K. De (a), A. K. Ghoshal (b), D. Pal (b), and A. K. Pal (b)

EPR and magnetic studies on single crystals of the dimeric copper (II) compound γ: bis (N-methyl salicylaldimine) Cu(II) down to 1.5 K reveal that each Cu(II) dimer is ferromagnetically exchange coupled having negligible interdimer exchange interaction. The magnetic properties are best described with C_{4v} ligand field symmetry around each Cu(II) ion. The principal axes of the susceptibility and the g-tensor are not strictly coincident at low temperature.

EPR und magnetische Untersuchungen an Einkristallen der dimeren Kupfer (II)-Verbindung γ: bis-(N-methylsalizylaldimin)–Cu(II) bis herab zu 1,5 K zeigen, daß jedes Cu(II)-Dimer ferromagnetisch austauschgekoppelt ist und eine vernachlässigbare interdimere Austauschwechselwirkung aufweist. Die magnetischen Eigenschaften lassen sich am besten mit C_{4v}-Ligandensymmetrie um jedes Cu(II)-Ion beschreiben. Die Hauptachsen des Suszeptibilitäts- und g-Tensoren sind nicht genau koinzident bei tiefen Temperaturen.

1. Introduction

In [1] we discussed temperature dependent g-shift and exchange interaction in β: bis(N-methyl salicylaldimine) copper(II) (β: CuMSal in brief).

Three-dimensional X-ray analysis [2] reveals that γ: CuMSal crystals contain eight formula units (four dimer units) in the orthorhombic cell with space group $P2_12_12_1$. The two molecules of the crystallographic asymmetric unit forming a dimer share two oxygen atoms. Each metal atom has a distorted planar coordination of two nitrogen and two oxygen atoms at distances ranging between 1.87 and 1.99 Å and each is displaced out of its coordinate plane, by 0.11 and 0.13 Å, respectively, towards the fifth donor oxygen atom which forms one of the basal corners of the copper in the companion molecule. X-ray distances between the copper ions within the dimer and those between the nearest magnetically non-equivalent Cu(II) ions are 3.35 and 7 Å, respectively.

The ligand fields around Cu(1) and Cu(2) may be taken to a good approximation to have either C_{4v} symmetry (square-pyramidal conformation) with Cu(1)–O(3) and Cu(2)–O(2) [2] as the symmetry axes or to have D_{4h} symmetry (square-planar conformation) with the normals to the planes [N(3)O(3)N(4)O(4)] or [N(1)O(1)N(2)O(2)] as the symmetry axes. The direction cosines (α, β, γ) of the relevant symmetry axis with respect to the crystallographic a, b, c axes in the cases of both C_{4v} and D_{4h} symmetries of the copper monomer units obtained from X-ray data are given in Table 1. It will be seen that in either symmetry the Cu(1) and Cu(2) paramagnetic units have almost identical orientations of their symmetry axes. The symmetry axes referred to each unit for C_{4v} and D_{4h} symmetries are oriented differently, the spatial angle between them being 12°.

[1]) Box 19059, UTA Sta. Arlington, TX 76019, USA.
[2]) 700032 Calcutta, India.

Table 1

Direction cosines of symmetry axes of copper(II) monomer units with respect to crystal-lographic a, b, c axes in γ:Cu(II)MSal (derived from X-ray results of Hall et al.) [2]

| direction cosines | C_{4v} symmetry axis | | D_{4h} symmetry axis (normal to CuO_2N_2 plane) | |
	Cu(1) — O(3)	Cu(2) — O(2)	Cu(1) O(1) N(1) O(2) N(2)	Cu(3) O(3) N(3) O(4) N(4)
α	−0.3874	−0.3904	+0.5649	+0.5676
β	+0.7049	+0.7022	−0.6676	−0.6696
γ	+0.5942	+0.5954	−0.4850	−0.4791

In principle, an EPR experiment is best suited to determine the symmetry as well as the orientation of the ligand field around each copper (II) paramagnetic unit in the single crystal, provided signals due to magnetically non-equivalent paramagnetic units could be resolved. Magnetic studies in conjunction with EPR enable proper elucidation of the dimeric structure in such compounds. So, the EPR and magnetic studies on single crystals (and also on powders) of γ:CuMSal were undertaken in the temperature range 1.5 to 300 K.

2. Experimental

2.1 Preparation of single crystals of γ:CuMSal

The compound was prepared by the reaction between methylamine and bis-salicyl-aldehydato copper (II) in ethyl alcohol. Brown rhombic plates of the γ-form were obtained by overnight crystallization from the filtrate left after the initial separation of the green α-form from the chloroform solution of the compound.

2.2 Mean magnetic susceptibility

The mean magnetic susceptibility was measured on the powdered compound with the help of a very sensitive Curie-type magnetic balance, but of robust design [3], provided with a cryostatic arrangement for measurements in the temperature range 77 to 300 K. The observed susceptibilities (χ_M) per gram-mole of Cu(II) ions at any temperature are corrected for diamagnetism of the molecule (χ_d). The square of the effective Bohr magneton number (p_f^2) per Cu(II) ion are calculated from

$$p_f^2 = \frac{3R}{N\mu_B^2}(\chi_M - \chi_d)T = \frac{3K_0}{N\mu_B^2}(\overline{K}T)\,, \tag{1}$$

where K_0 is the Boltzmann constant, μ_B the Bohr magneton, $\overline{K}$ the mean gram-molar susceptibility corrected for diamagnetism. p_f^2 values at different temperatures are given in Table 2. Although the p_f^2 values of γ:CuMSal fall in the range of values obtained for normal copper salts having negligible Cu–Cu exchange interaction, it can be readily seen from Table 2 that there occurs a gradual increase of the p_f^2 values with the decrease of temperature quite distinct from that obtained in copper acetate type antiferromagnetic dimer systems [5]. It will be later elaborated from theoretical fitting of p_f^2 at different temperatures that exchange coupling within a dimer in γ:CuMSal is of the ferromagnetic type.

Table 2

Principal crystalline anisotropies, mean square moments and mean susceptibilities of γ:Cu(II)MSal in the temperature interval 80 to 300 K

temperature (K)	$(\chi_b - \chi_c)$ ±0.1 (10^{-6} cgs units)	$(\chi_b - \chi_a)$ ±0.1 (10^{-6} cgs units)	p_i^2 ±0.0015 (cgs units)	$\overline{K}$ ±1.0 (10^{-6} cgs units)
300	71.01	146.0	3.504	1461
250	81.94	163.3	3.520	1760
200	98.21	189.2	3.548	2219
150	125.1	231.5	3.592	2996
100	179.3	311.2	3.684	4608
80	220.0	371.5	3.750	5863

2.3 Magnetic anisotropy

The principal crystalline anisotropies were measured in a very sensitive anisotropy balance [4] provided with a cryostatic arrangement. The crystalline anisotropies $(\chi_b - \chi_c)$ and $(\chi_b - \chi_a)$ were measured on a single crystal in the temperature range 77 to 300 K which are shown in Table 2. At room temperature, the anisotropy in the (010) plane, i.e., $(\chi_c - \chi_a)$, was also determined to provide a check on the anisotropy measurements in the (100) and (001) planes. It was found that $\chi_b > \chi_c > \chi_a$ in the whole temperature range (77 to 300 K) in which the experiments have been carried out. The three values of ionic anisotropy, $K_{||} - K_{\perp}$, were calculated from the principal crystalline susceptibility values using the three relations (2) and the X-ray data on the direction cosines of the approximate symmetry axes given in Table 1; i.e.

$$K_{||} - K_{\perp} = \frac{\chi_b - \chi_c}{\beta^2 - \gamma^2} = \frac{\chi_b - \chi_a}{\beta^2 - \alpha^2} = \frac{\chi_c - \chi_a}{\gamma^2 - \alpha^2}. \tag{2}$$

In either situation $K_{||} > K_{\perp}$ or $K_{\perp} > K_{||}$, agreement in the three values of $K_{||} - K_{\perp}$ as regards magnitude as well as sign could not be obtained on the basis of D_{4h} symmetry of each copper (II) monomer unit. On the other hand, the assumption of C_{4v} molecular symmetry is quite consistent with the three calculated values of $K_{||} - K_{\perp}$ (within 15%) from the experimentally determined principal crystalline anisotropies. It was found that $K_{||} > K_{\perp}$. Since the anisotropy is a very sensitive function of the

Table 3

Fitted direction cosines of the symmetry axis of copper(II) monomer units with respect to crystallographic a, b, c axes and the ionic anisotropies calculated from equations (2) in γ:Cu(II)MSal at different temperatures

temperature (K)	direction cosines use to obtain best fit in ΔK values			angle between Cu(1) — O(3) and derived symmetry axis (°)	ionic anisotropy $\Delta K = (K_{||} - K_{\perp})$ (10^{-6} cgs units)
	α	β	γ		
300	−0.3700	0.7253	0.5804	2.3	375
250	−0.3882	0.7196	0.5755	2.0	441.9
200	−0.4047	0.7130	0.5725	2.0	546.4
150	−0.4234	0.7046	0.5691	2.8	727.4
100	−0.4475	0.6939	0.5639	4.0	1101
80	−0.4563	0.6889	0.5629	4.5	1394

direction cosines (α, β, γ), a slight alteration in the values of the X-ray determined direction cosines, i.e. taking the orientation of the ionic symmetry axis to differ from that of the X-ray determined symmetry axis by about 2.3° (see Table 3), is sufficient to obtain an exact match among the three calculated $K_{\parallel} - K_{\perp}$ values. It is further noted that to effect exact fitting of the ionic anisotropy values $(K_{\parallel} - K_{\perp})$ at low temperatures, a slight alteration in the (α, β, γ) values obtained from the best fit at room temperature is also necessary at low temperatures, as shown in Table 3. This may be due to small orientational changes in the dimeric clusters at different temperatures.

3. EPR

EPR measurements have been made with the help of a transmission-type K-band EPR spectrometer set up (by the author with his co-workers) in this laboratory in the principal planes (001), (010), and (100) at room temperature and with a Bruker Physik X-band EPR spectrometer on a different specimen. Surprisingly only one resonance signal devoid of any structure was observed in the three principal crystal planes in all the single crystal specimens although the dimeric structure appeared in frozen solution EPR spectra of γ:Cu(II)MSal taken at 77 K [6]. The first derivative linewidths of the EPR signals in these planes were found to be in the range 50 to 600 G. Similar observations were made in copper (II) diethyldithiocarbamate, $Cu(dtc)_2$, where the Cu–Cu separations within the dimers are 3.59 Å. In $Cu(II):Zn(dtc)_2$ crystals [7 to 9] dimeric EPR spectra have been obtained whereas it remained unobserved in $Cu(dtc)_2$ crystals [10]. The existence of ferromagnetic dimers in $Cu(dtc)_2$ has also been established from mean magnetic susceptibility studies [11]. It is significant that the fine structure constant, i.e. the zero-field splitting parameter D (which consists of a pseudo-dipolar term originating from exchange interaction within the dimer and a dipolar interaction term between copper(II) ions of different dimers) is found to be very much smaller in $Cu:Zn(dtc)_2$ (0.028 cm^{-1}) than that in copper acetate monohydrate [5] (≈ 0.3 cm^{-1}).

Moreover, signals due to magnetically non-equivalent Cu(II) complexes could not be resolved in any plane of the single crystal; and, therefore, the experimentally determined g-values correspond to crystalline g-values. Under these circumstances the ionic g-values ($g_{\parallel}$ and $g_{\perp}$) can only be derived from the crystalline g-values with the help of X-ray determined angular coordinates (α, β, γ) of the symmetry axes of the copper(II) monomer units using the following equations:

$$g_{\parallel}^2 - g_{\perp}^2 = (g_b^2 - g_c^2)/(\beta^2 - \gamma^2) = (g_b^2 - g_a^2)/(\beta^2 - \alpha^2) = (g_c^2 - g_a^2)/(\gamma^2 - \alpha^2) \,, \quad (3)$$

$$g_{\parallel}^2 + 2g_{\perp}^2 = g_a^2 + g_b^2 + g_c^2 \,. \quad (4)$$

The maximum and minimum values of g in each principal plane correspond to two of three principal crystalline g-values (g_a, g_b, g_c). These, as well as the χ_a, χ_b, and χ_c directions coincide with the crystallographic a, b, and c axes in an orthorhombic crystal like γ:CuMSal. It has been found that the three values of $g_{\parallel}^2 - g_{\perp}^2$ obtained from the principal crystalline g-values using the three relations (3) and the fitted direction cosines of the C_{4v} symmetry axes of the copper complexes (see Table 3) obtained from magnetic anisotropy data are quite consistent with each other. The principal crystalline and ionic g-values at 300 K are given in Table 4. X-band EPR spectra were also performed on the powdered sample at room temperature, 77, 20, and 1.5 K through the kind courtesy of Dr. H. Lange and Dr. W. Gehlhoff of Akademie der Wissenschaften der DDR, Berlin. All the spectra showed characteristic features of powdered EPR spectra with orthorhombic g-tensor and were analysed according

Table 4

Crystalline and ionic g-values along with the fitted direction cosines of the ionic symmetry axis in γ:(Cu(II) MSal) in the temperature range 300 to 1.5 K

tempera-ture (K)	g_a	g_b	g_c	$g_{||}$	$g_\perp$	α	β	γ
300	2.067 ±0.002	2.163 ±0.002	2.117 ±0.002	2.274	2.033	−0.3700	0.7253	0.5804
77	2.07 ±0.005	2.165 ±0.005	2.12 ±0.005	2.280	2.033	−0.3767	0.7208	0.5818
20	2.07 ±0.005	2.165 ±0.005	2.12 ±0.005	2.280	2.033	−0.3767	0.7208	0.5818
1.5	2.035 ±0.005	2.175 ±0.005	2.11 ±0.005	2.294	2.007	−0.300	0.7536	0.5849

to the method of Johnston and Hecht [12]. The program was first standardized to fit the EPR powder spectra at room temperature with the principal crystalline g-values obtained from the single crystal study. With some alteration in the values of the linewidths W_x, W_y, W_z obtained at room temperature the spectra at 77 and 20 K could be fitted with the g-values obtained at room temperature (Table 4). The principal crystalline g-values obtained at 1.5 K were however found to be different from those obtained at other temperatures (Table 4). The corresponding principal ionic g-values $g_{||}$ and $g_\perp$ could be derived using (3) and (4) and using α, β, γ as obtained by fitting the magnetic data at room temperature (Table 4). Some alteration in the above values of α, β, γ was found necessary to obtain consistent values of $g_{||}^2 - g_\perp^2$ at 1.5 K using equation (3). It is seen from Table 3 that the values of α, β, γ obtained by fitting the magnetic anisotropy data vary with temperature in the range 300 to 77 K. On the other hand, the orientation of the g-tensor changes significantly only at 1.5 K. Slight deviation in the orientation of the g-tensor observed at 77 to 20 K (Table 5) from the room temperature values may be due to some error involved in the extraction of the g-values from powdered EPR spectra. The angle between corresponding g-axes

Table 5

Best fitting of observed ionic anisotropy and mean square moment of γ:Cu(II)MSal at different temperatures with the following ligand field parameters: $g_{||} = 2.274$, $(hf)_{||} = 36.5 \times 10^{-6}$ cgs, $J = +29.3$ cm^{-1}, observed $g_\perp = 2.033$, $(hf)_\perp = 1.4 \times 10^{-6}$cgs $\theta = 0$ cm^{-1}

tempera-ture (K)	$(K_{||} \rightarrow K_\perp)$ (10^{-6} cgs units)		p_f^2	
300	375	(372.0)	3.504	(3.504)*)
250	441.9	(441.6)	2.520	(3.520)
200	546.4	(547.5)	3.548	(3.547)
150	727.4	(727.8)	3.592	(3.592)
100	1101	(1101.5)	3.684	(3.684)
80	1394	(1392)	3.750	(3.749)

*) Values within the parenthesis are calculated from (9) and (10) using the above values of J, $(hf)_{||}$ and $(hf)_\perp$.

at 300 and 1.5 K is 4°. Thus the orientation of the principal axes of the ionic g-tensor and the susceptibility tensor are not strictly coincident at low temperature in this crystal.

4. Theoretical Considerations

The wave functions for Cu(II) under C_{4v} ligand field symmetry considering 'd–p, s' admixture are

$$
\begin{aligned}
(^2B_1) \quad & \psi_1 = |x^2 - y^2\rangle \,, \\
(^2A_1) \quad & \psi_2 = p_2|z^2\rangle + \gamma_2 p_2|z\rangle + \alpha p_2|S\rangle \,, \\
& \psi_3 = p_3|xz\rangle + \gamma_3 p_3|x\rangle \,, \\
(^2E) \quad & \psi_3' = p_3|yz\rangle + \gamma_3 p_3|y\rangle \,, \\
& \psi_4 = |xy\rangle \,.
\end{aligned}
\tag{5}
$$

The p_i's and the γ_i's denote the extent of overlap of the ligand wave functions $|x\rangle$ etc., to the d-wave functions of the copper(II) ion.

$^2B_1$ is usually the ground state [13]. Each Cu(II) ion within a dimer is also coupled by exchange interaction of the form (J being the intradimer exchange integral)

$$
\mathcal{H}_{ex} = -J S_1 \cdot S_2 \,.
\tag{6}
$$

The magnetic properties of each of the copper(II) ion (in a dimer) having the wave functions given by (5) can be described by the following Hamiltonian:

$$
\mathcal{H} = \lambda_d L \cdot S + \mu_B H \cdot (L + 2S) \,.
\tag{7}
$$

$\lambda_d = -829 \ \text{cm}^{-1}$ is the spin–orbit coupling constant for the free Cu(II) ion. Following essentially the treatment of Bose et al. [14] and the spin Hamiltonian technique of Abragam and Pryce [15] up to second-order perturbation the following expressions for p_f^2 and $K_{\|} - K_{\perp}$ could be derived with the help of (1) and (8):

$$
\bar{K} = \frac{K_{\|} + 2K_{\perp}}{3} \,,
\tag{8}
$$

$$
p_f^2 = (g_{\|}^2 + 2g_{\perp}^2)/(3 + e^{-J/K_0 T}) + [(hf)_{\|} + 2(hf)_{\perp}]/3 \,,
\tag{9}
$$

$$
K_{\|} - K_{\perp} = \frac{N\mu_B^2}{K_0 T} (g_{\|}^2 - g_{\perp}^2)/(3 + e^{-J/K_0 T}) + [(hf)_{\|} - (hf)_{\perp}]/3 \,.
\tag{10}
$$

Where the temperature independent high frequency terms $(hf)_{\|}$ and $(hf)_{\perp}$ and $g_{\|}$, $g_{\perp}$ are given by

$$
g_{\|} = 2[1 - 4R_{\|}k_{\|}\lambda_d/(E_{B_2} - E_{B_1})] \,,
\tag{11}
$$

$$
g_{\perp} = 2[1 - 2R_{\perp}k_{\perp}\lambda_d/(E_E - E_{B_1})] \,,
\tag{12}
$$

$$
(hf)_{\|} = -(g_{\|} - 2) N\mu_B^2 R_{\|}/2\lambda_d k_{\|} \,,
\tag{13}
$$

$$
(hf)_{\perp} = -(g_{\perp} - 2) N\mu_B^2 R_{\perp}/2\lambda_d k_{\perp} \,.
\tag{14}
$$

$R_{\|}$, $k_{\|}$ etc. in (11) to (14) are known as the covalent spin–orbit and orbital reduction factors.

5. Results of Fitting the Magnetic Data and Discussion

The values of p_f^2 and $K_{\|} - K_{\perp}$ at different temperatures and also $g_{\|}$ and $g_{\perp}$ for CuMSal are known from experiment (Tables 2 to 4). These data have been fitted to (9) and (10) by the least-squares fitting method using IBM 370 computer. The best

fit values of J, $(hf)_{||}$, $(hf)_{\perp}$ so obtained are given in Table 5 along with the corresponding calculated values of $\bar{K}_{||} - K_{\perp}$ and p_f^2. They are found to agree quite well with the experimental values. A Weiss term θ which accounts for the interdimer exchange interactions may also be present, and the temperature term should be replaced by $T + \theta$. However, it was seen that incorporation of θ did not lead to a better fitting in the temperature range studied. The values of $R_{||}/k_{||}$ and $R_{\perp}/k_{\perp}$ were found to be 0.86 and 0.27, respectively with the help of (13) and (14). However, in the absence of spectroscopic data on γ:Cu(II)MSal, a unique estimation of the covalency parameters ($k_{||}$, $R_{||}$ etc.) has not been possible, even with the help of equations (11) and (12). The somewhat abnormal value of $R_{\perp}/k_{\perp}$ may be due to the fact that the principal axes of the susceptibility and the g^2 tensor are not strictly coincident as found by experiment — a fact which is not considered in deriving equations (13) and (14).

It is evident from our analysis of the magnetic data, that the symmetry of the ligand field around each monomer unit of a copper dimer in γ:Cu(II)MSal, to a good approximation, is C_{4v}. In consequence the origin of the ferromagnetism of the copper dimers (J is positive and therefore the ground state is a triplet) can be reasonably sought for in the superexchange mechanism through terminal oxygen ligands similar to the $90°$ interaction proposed by Anderson (1950) [16] and Goodenough (1955) [17], the direct copper–copper exchange mechanism, (Cu–Cu separation is large, i.e. 3.3 Å) being of secondary importance. (In α:Cu(II)MSal [18] the Cu:Cu separation is 3.3 Å and the direct Cu–Cu exchange is found to be 2.24 cm^{-1}). Also the analysis shows that interdimer exchange is negligible.

The situation in the present case may be compared to that in well-studied copper acetate monohydrate, which is composed of strong antiferromagnetically coupled dimers. In the latter case, unlike the former, although there are four superexchange paths (Cu–O–C–O–Cu) through acetate bridges within the dimer, direct copper–copper exchange interaction ($J = 300$ cm^{-1} [14]) presumably plays the major role in the antiferromagnetism of the copper dimer, the Cu–Cu separation being small (2.64 Å) [19]. This has also been corroborated from the theoretical correlation of magnetic and spectral data of copper acetate monohydrate [14]. Further, we have noticed an increase in the intensity (approximately six times) of the EPR spectrum in γ:CuMSal at 20 K over that at room temperature. With ferromagnetic exchange interaction (with positive J in equation (6)) the triplet $S = 1$ is the ground state (energy $= -J/4$) and is separated from the singlet $S = 0$ excited state (energy $= 3J/4$) by an amount J. So with the lowering of temperature the population of the triplet state increases and as a result the intensity of the EPR signal and the p_f^2 should increase as the temperature is decreased unlike in the case of Cu(Ac)$_2$, H$_2$O type antiferromagnetic compounds, where J is negative. The reason for the absence of dimeric hyperfine structures in undiluted γ:CuMSal unlike Cu(Ac)$_2$ · H$_2$O is not clear at present. Comparing Table 4 with Table 1 of our previous paper [1] on β:CuMSal we find that in γ:CuMSal there is no significant shift of the g-values in the temperature range 20 to 300 K, unlike that in β:CuMSal. This ensures that the vibronic mechanism which gives rise to the g-shift in β:CuMSal is unimportant in γ:CuMSal. There is, however, a small g-shift at 1.5 K. The origin of this shift is not clear to us at present.

References

[1] D. K. DE, Ph. D. Thesis, Calcutta University 1980.
[2] D. HALL, S. V. SHEAT, and T. N. WATERS, Chem. Commun. 436 (1966); J. Chem. Soc. A460 (1968).
[3] A. BOSE, S. K. DUTTA ROY, P. K. GHOSH, and S. MITRA, Indian J. Phys. 37, 505 (1963).
[4] D. GUHA THAKURATA and D. MUKHOPADHYAY, Indian J. Phys. 40, 69 (1966).

[5] B. BLEANEY and K. D. BOWERS, Proc. Roy. Soc. **A214**, 451 (1952).
[6] M. CHIKIRA and T. ISOBE, Bull. Chem. Soc. Japan **45**, 3006 (1972).
[7] R. K. COWSIK, G. RANGARAJAN, and R. SRINIVASAN, Chem. Phys. Letters **8**, 136 (1971).
[8] R. K. COWSIK and R. SRINIVASAN, Pramana **1**, 177 (1973).
[9] S. A. ALTSHULER, R. KIRMSE, and B. V. SOLOVOEV, J. Phys. C **8**, 1907 (1975).
[10] A. K. PAL, S. N. MITRA, and P. SENGUPTA, J. chem. Phys. **48**, 5219 (1968).
[11] J. F. VILLA and W. E. HATFIELD, Inorg. Chem. **10**, 2038 (1971).
[12] T. S. JOHNSTON and H. G. HECHT, J. Mol. Spectr. **17**, 98 (1965).
[13] S. T. SPEES, Jr., J. R. PERUMAREDDI, and A. W. ADAMSON, J. phys. Chem. **72**, 1822 (1968).
[14] A. BOSE, R. N. BAGCHI, and P. SENGUPTA, Indian J. Phys. **42**, 55 (1968).
[15] A. ABRAGAM and M. H. L. PRYCE, Proc. Roy. Soc. **A205**, 135 (1951).
[16] P. W. ANDERSON, Phys. Rev. **79**, 350 (1950).
[17] J. B. GOODENOUGH, Phys. Rev. **100**, 564 (1955).
[18] R. R. BARTKOWSKI and B. MOROSIN, Phys. Rev. B **6**, 4209 (1972).
[19] J. N. VAN NIEKERK and F. R. L. SCHOENING, Acta cryst. **6**, 227 (1953).