

Ligand Replacement Reactions in
Transition Metal Complexes: Part IV—
Replacement of Coordinated Water by
Some N&S Donors in Hydrated Iron(II),
Cobalt(II) & Nickel(II)
Nitrosopentacyanoferrates(II)

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Treatment of hexaaquoiron(II), hexaaquonickel(II) and tetraaquocobalt(II) nitrosopentacyanoferrates(II) with various nitrogen and sulphur donors results in replacement of coordinated water molecules by the donor molecules. The anion i.e. nitrosopentacyanoferrate(II) remains undisturbed in the products. Analytical and physicochemical data suggest octahedral structures for all iron(II) and nickel(II) complexes, and tetrahedral structures for four coordinated and octahedral structures for six coordinated cobalt(II) complexes.

In our earlier publications¹⁻³ we have reported a number of solid products obtained by the replacement of coordinated water molecules from copper(II) and nickel(II) complexes of aliphatic, aromatic or heterocyclic amines, diamines or schiff bases and a few oximes such as furan-2-carboxaldoxime. The earlier results showed that the replacement of one or two water molecules was easy and could be achieved by using any ligand. But the remaining water molecules could be removed only with the help of di-, tri- or tetraamines. In the present note, we report the results of a similar type of study on hydrated iron(II), cobalt(II) and nickel(II) complexes using different kinds of amines; but, the specific anion chosen is the nitrosopentacyanoferrate(II) which is itself a low-spin octahedral complex of iron(II). The isolated solid complexes have been fully characterised using analytical, molar conductance, TGA, magnetic, infrared and electronic spectra data (Table 1).

A known weight of aquometal(II) nitrosopentacyanoferrate(II) was suspended in methanol, an excess amount of ligand (dissolved in methanol) was added to it slowly, and the mixture was continuously stirred. After the addition of the ligand was completed, the reaction mixture was further stirred for a few more hours till a coloured solution was obtained. The

complexes were obtained in crystalline form by repeated treatment with ethanol, acetone and petroleum ether and by keeping the solution at low temperature.

The molar conductance values of the complexes measured in nitrobenzene correspond to 1:1 electrolytes. It is thus suggested that the nitrosopentacyanoferrate(II) ion remains outside the coordination sphere of metal(II) ion. These results are supported by infrared and TGA data as follows. (i) The IR frequencies due to cyanide (2100 cm^{-1}) and nitrosonium (1940 cm^{-1}) ions remain unchanged in the spectra of the products as compared with those in the spectra of the products as compared with those in the parent complex⁴⁻⁶, aquometal(II) nitrosopentacyanoferrate(II).

(ii) The coordination of water is indicated by the TGA and infrared data. In all the complexes a definite loss in mass occurs between 60 and 80°C and this corresponds to the presence of different number of lattice water molecules. In addition, the complexes show a further mass loss between 110 and 300°C (the range in which the coordinated water and amines are lost simultaneously). All the five cyanide ions and NO are lost in the range 300-600°C; thereafter, probably the metal nitride is formed and the weight remains constant from 600 to 800°C.

In confirmation of this a strong broad band appears around 3500 cm^{-1} , which has two specific components at 3510 and 3402 cm^{-1} . The former is the νOH due to lattice water and latter is the coordinated νOH shifted^{7,8} by some 100 cm^{-1} .

(iii) The coordination of ammonia and amines is shown by a distinct lowering of νNH , while the coordination of nitroanilines, 2,2'-dipyridyl and 1,10-phenanthroline is indicated by the positive shifts of $\text{C}=\text{C}$, $\text{C}=\text{N}$, ring stretching frequencies and the presence of two out of the three deformation modes^{9,12} at 1170 and 1980 cm^{-1} .

(iv) The thiourea molecule is coordinated through sulphur and acts as a monodentate ligand¹³⁻¹⁵.

The magnetic moments of the complexes were determined by the Gouy's method. The iron(II)thiourea complex has a μ_{eff} value of 5.33 B.M., corresponding to four unpaired electrons, while the dipy and phen complexes have μ_{eff} values of 1.06 B.M. The Co(II) complexes with ammonia and aliphatic amines are tetraordinated while rest of the complexes are hexacoordinated. It is not possible to distinguish between the two geometries on the basis of room temperature μ_{eff} values; hence, magnetic

Table I—Analytical and Magnetic Data of the Complexes

| Complex | Found (Calc.), % | | | | $\mu_{\text{eff.}}$ (B.M.) |
|--|------------------|------------------|----------------|------------------|-------------------------------|
| | M | C | H | N | |
| 1 $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 28.92 (29.41) | 15.52 (15.80) | — — | 22.36 (22.12) | 5.12 |
| 2 $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3][\text{Fe}(\text{CN})_5\text{NO}^+].7\text{H}_2\text{O}$ | 13.33 (13.79) | 52.31 (51.87) | 4.22 (4.69) | 20.22 (20.13) | 1.09 |
| 3 $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3][\text{Fe}(\text{CN})_5\text{NO}^+].7\text{H}_2\text{O}$ | 11.42 (11.91) | 51.99 (52.90) | 4.36 (4.05) | 17.37 (17.91) | 1.06 |
| 4 $[\text{Fe}(\text{CH}_4\text{N}_2\text{S})(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+].3\text{H}_2\text{O}$ | 23.22 (22.71) | 15.02 (14.65) | 3.74 (4.07) | 22.72 (22.77) | 5.53 |
| 5 $[\text{Co}(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 15.78 (16.10) | 17.82 (17.32) | 2.00 (2.30) | 23.86 (24.22) | 4.46 |
| 6 $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_5\text{NO}^+].4\text{H}_2\text{O}$ | 15.83 (15.39) | 17.00 (16.55) | 3.18 (3.30) | 30.43 (30.86) | 4.53 |
| 7 $[\text{Co}(\text{CH}_3\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].2\text{H}_2\text{O}$ | 14.30 (14.11) | 18.85 (18.20) | 3.06 (3.79) | 24.28 (24.75) | 4.71 |
| 8 $[\text{Co}(\text{C}_2\text{H}_5\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 14.62 (13.62) | 19.85 (20.49) | 3.66 (4.14) | 24.02 (23.92) | 4.77 |
| 9 $[\text{Co}(n\text{-C}_3\text{H}_7\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].3\text{H}_2\text{O}$ | 13.01 (12.64) | 21.65 (21.75) | 4.42 (4.75) | 22.61 (22.18) | 4.83 |
| 10 $[\text{Co}(i\text{-C}_3\text{H}_7\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].2\text{H}_2\text{O}$ | 13.64 (13.18) | 22.06 (22.68) | 4.12 (4.48) | 22.78 (23.12) | 4.69 |
| 11 $[\text{Co}(n\text{-C}_4\text{H}_9\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].3\text{H}_2\text{O}$ | 12.72 (12.25) | 23.05 (23.72) | 4.30 (5.04) | 21.00 (21.50) | 4.84 |
| 12 $[\text{Co}(i\text{-C}_4\text{H}_9\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].\text{H}_2\text{O}$ | 13.66 (13.30) | 25.25 (25.75) | 4.08 (4.52) | 22.78 (23.34) | 4.63 |
| 13 $[\text{Co}(n\text{-C}_5\text{H}_{11}\text{NH}_2)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].3\text{H}_2\text{O}$ | 11.40 (11.88) | 24.85 (25.56) | 5.06 (5.32) | 21.21 (20.85) | 4.84 |
| 14 $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{H}_2\text{O})][\text{Fe}(\text{CN})_5\text{NO}^+].4\text{H}_2\text{O}$ | 12.03 (11.68) | 17.60 (17.55) | 4.98 (5.01) | 23.47 (23.39) | 5.11 |
| 15 $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_5\text{NO}^+].4\text{H}_2\text{O}$ | 11.11 (11.33) | 18.95 (19.48) | 4.66 (5.27) | 23.15 (22.72) | 5.03 |
| 16 $[\text{Co}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_5\text{NO}^+].8\text{H}_2\text{O}$ | 10.20 (9.69) | 18.85 (18.77) | 5.51 (6.07) | 22.25 (21.87) | 5.52 |
| 17 $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_5\text{NO}^+].8\text{H}_2\text{O}$ | 9.80 (9.29) | 21.40 (21.98) | 6.06 (6.32) | 22.86 (23.29) | 5.33 |
| 18 $[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2)_3][\text{Fe}(\text{CN})_5\text{NO}^+].2\text{H}_2\text{O}$ | 7.78 (7.18) | 54.45 (53.94) | 3.75 (3.59) | 21.30 (21.56) | 2.11 |
| 19 $[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)_3][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 7.20 (6.85) | 59.80 (60.41) | 3.20 (2.94) | 21.08 (20.61) | 2.03 |
| 20 $[\text{Co}(\text{CH}_4\text{N}_2\text{S})(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+].3\text{H}_2\text{O}$ | 11.78 (11.29) | 14.03 (14.56) | 3.78 (4.04) | 22.33 (22.63) | 4.84 |
| 21 $[\text{Ni}(\text{C}_6\text{H}_5\text{NH}_2)(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 12.44 (12.82) | 29.12 (28.86) | 3.66 (3.71) | 21.33 (21.41) | 3.06 |
| 22 $[\text{Ni}(\text{C}_8\text{H}_{11}\text{N})(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 12.34 (12.09) | 31.74 (32.14) | 3.78 (4.32) | 19.66 (20.18) | 3.10 |
| 23 $[\text{Ni}(\text{C}_{10}\text{H}_{15}\text{N})(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+]$ | 11.02 (11.45) | 34.60 (35.12) | 4.31 (4.87) | 18.66 (19.11) | 3.22 |
| 24 $[\text{Ni}(o\text{-C}_6\text{H}_4\text{N}_2\text{O}_2)(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_5\text{NO}^+].\text{H}_2\text{O}$ | 11.23 (11.68) | 25.66 (26.28) | 2.77 (3.16) | 21.80 (22.18) | 3.20 |
| 25 $[\text{Ni}(m\text{-C}_6\text{H}_4\text{N}_2\text{O}_2)(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_5\text{NO}^+].\text{H}_2\text{O}$ | 12.02 (11.88) | 25.88 (26.28) | 3.50 (3.18) | 22.60 (22.28) | 3.22 |
| 26 $[\text{Ni}(p\text{-C}_6\text{H}_4\text{N}_2)(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_5\text{NO}^+].2\text{H}_2\text{O}$ | 11.44 (11.28) | 24.86 (25.37) | 3.03 (3.45) | 21.06 (21.51) | 3.24 |
| 27 $[\text{Ni}(\text{CH}_4\text{N}_2\text{S})(\text{H}_2\text{O})_5][\text{Fe}(\text{CN})_5\text{NO}^+].\text{H}_2\text{O}$ | 12.34 (12.29) | 15.10 (15.69) | 2.93 (3.48) | 24.00 (24.40) | 3.05 |

moments at two lower temperatures (at 257 K and 143 K) for four complexes of tetraordinated category were measured and the values observed are similar to that found at room temperature (303 K). Since no change in the values is seen, it is consistent with the presence of ground state A and a tetrahedral structure, for which μ_{eff} is independent of temperature¹⁶. For nickel(II) complexes the values in the range 3.02-3.20 B.M. are obtained which are characteristic of spin-free octahedral configuration.

In iron(II) only one allowed transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ is seen in the form of one main band at 18.00 kK, with two shoulders at 10.50 kK and 8.00 kK, which are due to ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and ${}^1A_{1g} \rightarrow {}^3T_{2g}$ spin-forbidden transitions^{17,18}. In 2,2'-dipyridyl and 1,10-phenanthroline complexes, the band due to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ is present at 12.20 kK. In thiourea complex a single band at 10.52 kK is present due to ${}^5T_{2g} \rightarrow {}^5E_g$ transition of high-spin iron(II)^{19,20}. The values of Dq and B for these complexes are 821 cm^{-1} and 1000 cm^{-1} respectively.

The cobalt(II) complexes of ammonia and aliphatic amines are tetrahedral as is clear from their μ_{eff} values at low temperature. These, however, give a number of bands due to spin-forbidden ${}^4A_2 \rightarrow {}^2A_1$ transition in the range 25.00-20.00 kK: since the nitrosopentacyanoferrate(II) bands also occur in this range the assignment of bands is not very accurate²¹. The ν_3 transition ${}^4A_2(F) \rightarrow {}^4T_1(P)$ splits into three components at 17.00 kK, 16.50 kK and 14.50 kK. This splitting is due to spin-orbit coupling effect, an essential feature of tetrahedral cobalt(II). The ν_2 transition ${}^4A_2(F) \rightarrow {}^4T_1(F)$ occurring in the region 10.06-6.00 kK also has a multiple character with bands at 6.60, 6.34 and 5.81 kK. Since the complex is a mixed cation $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ or $[\text{Co}(\text{am})(\text{H}_2\text{O})_3]^{2+}$ the symmetry is lowered from true T_d to C_{2v} . The Dq , B and β values are in the same range as for the tetrahedral complexes^{22,23}.

The complexes of ethylenediamine, propylenediamine, diethylenetriamine and triethylenetetramine are octahedral as these give two bands centered around 20.00 kK and 9.99 kK. These are assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) transitions respectively. The ν_3 band is split into two components due to the lowering of symmetry. The assignment of the 20.00 kK component is difficult as it is obscured by

the nitrosopentacyanoferrate(II) band; the other component at 18.00 kK has, however, been seen in some of the complexes. The bands in the range 8.50-7.20 kK have been assigned as ν_1 . The Dq and the B values are around 950 and 1000 cm^{-1} justifying the assignment of pseudo-octahedral geometry²⁴.

The nickel(II) complexes are also spin-free hexacoordinated giving ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) bands at 27.00, 16.00 and 9.50 kK respectively. In this case also the ν_2 band was assigned with difficulty due to its overlapping with nitrosopentacyanoferrate(II) band. Since the coordination sphere of complexes is $[\text{Ni}(\text{H}_2\text{O})_5\text{L}]^{2+}$, the local symmetry D_{4h} has been used. The Dq , B , β and ν_2/ν_1 values correspond to an octahedral geometry^{25,26}.

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