

Cobalt(II) and Nickel(II) Complexes with the Propylene-bridged Tripod Ligand Tris-(3-dimethylaminopropyl)amine (Donor Set N₄).

By A. Dei and R. Morassi,* Istituto di Chimica Generale ed Inorganica, Università di Firenze; Laboratorio C.N.R., 41, Via Jacopo Nardi, 50132 Firenze, Italy

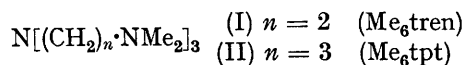
The tripod ligand tris-(3-dimethylaminopropyl)amine (Me₆tpt, donor set N₄) has been synthesized. It forms high-spin cobalt(II) and nickel(II) complexes of general formula [M(L)X]BPh₄ (M = Co, Ni; X = Cl, Br, I). A tetrahedrally distorted trigonal bipyramidal structure is attributed in the solid state to both the cobalt(II) and nickel(II) complexes, which are isomorphous for any given halogen. A more regular five-co-ordinate structure is achieved by the nickel(II) complexes in solution, whereas the cobalt(II) complexes assume a pseudo-tetrahedral structure with N₃X donor set in solvents of low polarity. A complex with formula [CoL](BPh₄)₂ has also been isolated: this is believed to contain a pseudo-tetrahedral [CoL]²⁺ cation. The critical steric requirements of the Me₆tpt ligand, with respect to previously reported tetramine tripod ligands, are discussed.

THE 'tripod' ligand tris-(2-aminoethyl)amine (tren, donor set N₄) reacts with bivalent ions of the first-transition series to give both octahedral complexes (with Mn, Fe, and Ni)¹ and five-co-ordinate complexes (with Co, Cu, and Zn);² the analogous *N*-methylated ligand tris-(2-dimethylaminoethyl)amine (Me₆tren, I) gives only five-co-ordinate [M(ligand)X]X complexes with all bivalent ions from Cr^{II} to Zn^{II}.³

The latter compounds, which are all isomorphous, have been found by *X*-ray analysis to exhibit a trigonal

bipyramidal geometry in which the angle N(apical)-M-N(equatorial) ranges from 81° to 85°, apparently on account of the shortness of the ethylenic linkages.⁴

In order to investigate in which way lengthening all three 'legs' in Me₆tren should affect the complexing ability of the ligand, we have synthesized tris-(3-dimethylaminopropyl)amine (Me₆tpt, II).



Here we report on the cobalt(II) and nickel(II) complexes formed by the Me₆tpt ligand.

¹ C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887; D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 1958, 346; S. E. Rasmussen, *Acta Chem. Scand.*, 1959, **13**, 2009; P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 1963, 3589.

² (a) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, 1967, **6**, 1261; (b) P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 724; P. C. Jain, E. C. Lingafelter, and P. Paoletti, *J. Amer. Chem. Soc.*, 1968, **90**, 519.

³ M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41, 1150; M. Ciampolini, N. Nardi, and G. P. Speroni, *Co-ordination Chem. Rev.*, 1966, **1**, 222; M. Ciampolini, *Chem. Comm.*, 1966, 47.

⁴ M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 955; M. Di Vaira and P. L. Orioli, *Acta Cryst.*, 1968, **B 24**, 595, 1269.

RESULTS AND DISCUSSION

Complexes with general formula $[M(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ ($M = \text{Co}, \text{Ni}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been obtained. Analytical and magnetic data are reported in Table 1. The complexes are moisture-sensitive; their solutions in *o*-dichlorobenzene or nitroethane are stable in the

lower frequencies in the $[\text{Ni}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ series, and (iii) the relative intensity of corresponding bands is different within the two series of complexes (Figure 1).

From these results, it may be concluded that the $[\text{Ni}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ complexes are five-co-ordinate like their Me_6tren analogues [point (i)], but their structure

TABLE 1
Analytical and magnetic data for the complexes

Compound	Colour	Found (%)				Required (%)				μ_{eff} (B.M.) ^a
		C	H	N	Metal	C	H	N	Metal	
(1) $[\text{Ni}(\text{Me}_6\text{tpt})\text{Cl}]\text{BPh}_4$	Purple	67.9	8.1	8.2	8.3	68.29	8.22	8.16	8.56	3.25 (21)
(2) $[\text{Ni}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$	Purple	64.5	8.2	7.4	7.8	64.11	7.72	7.67	8.04	3.23 (22)
(3) $[\text{Ni}(\text{Me}_6\text{tpt})\text{I}]\text{BPh}_4$	Purple	60.8	7.5	7.0	7.4	60.24	7.26	7.20	7.55	3.45 (22)
(4) $[\text{Co}(\text{Me}_6\text{tpt})\text{Cl}]\text{BPh}_4$	Violet	67.5	8.4	7.7	8.0	68.27	8.22	8.16	8.58	4.31 (23)
(5) $[\text{Co}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$	Blue-violet	63.7	8.4	7.2	7.7	64.09	7.72	7.67	8.06	4.26 (23)
(6) $[\text{Co}(\text{Me}_6\text{tpt})\text{I}]\text{BPh}_4$	Blue-violet	60.7	7.8	7.0	7.3	60.22	7.26	7.20	7.57	4.39 (22)
(7) $[\text{Co}(\text{Me}_6\text{tpt})](\text{BPh}_4)_2$	Magenta	78.0	8.2	6.0	6.1	78.01	7.90	5.78	6.08	4.41 (23)

^a Temp. (°C) in parentheses.

TABLE 2
Conductometric and spectrophotometric data for the complexes

Compound	Λ_{M} ^a ($\text{cm}^2 \text{ohm}^{-1}$)	State ^b	Absorption max. (kK) with ϵ_{molar} for soln. in parentheses ^c
(1) $[\text{Ni}(\text{Me}_6\text{tpt})\text{Cl}]\text{BPh}_4$	49	R	5.9br, 9.5sh, 11.0sh, 12.6, 18.4sh, 20.6
(2) $[\text{Ni}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$	46	R	8.0vbr (13), 12.0sh, 14.1 (30), 24.2 (91)
(3) $[\text{Ni}(\text{Me}_6\text{tpt})\text{I}]\text{BPh}_4$	51	R	5.8br, 9.3, 10.9sh, 12.7, 18.1sh, 19.6
(4) $[\text{Co}(\text{Me}_6\text{tpt})\text{Cl}]\text{BPh}_4$	50	R	6.9vbr (14), 11.7sh, 14.5 (47), 20.0sh, 24.6 (166)
(5) $[\text{Co}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$	77	R	5.7br, 9.1, 10.8sh, 12.7, 17.0sh, 18.9
(6) $[\text{Co}(\text{Me}_6\text{tpt})\text{I}]\text{BPh}_4$	120	R	6.6vbr (14), 11.7 (19), 14.6 (56), 20.5sh, 24.8 (212)
(7) $[\text{Co}(\text{Me}_6\text{tpt})](\text{BPh}_4)_2$	—	R	7.5sh, 8.5, 11.2, 17.3, 18.2sh
		D	6.4 (20), 7.7 (30), 10.4 (25), 15.9sh, 16.4 (195), 17.6 (150)
		R	7.4sh, 8.5, 11.0, 17.0, 18.1sh
		D	5.9 (24), 7.3 (39), 9.9 (34), 16.0 (265), 16.9sh
		R	7.2sh, 8.5, 10.6, 16.8, 18.0
		D	5.8 (15), 7.2 (28), 9.8 (30), 14.9sh, 15.6 (145), 16.4 (147), 16.9sh
		R	8.2, 10.5sh, 11.3, 18.2, 19.0sh

^a For ca. 10^{-3}M -soln. in nitroethane at 20°. Reference value: $[\text{Bu}_4\text{N}]\text{BPh}_4$, 58. ^b R = Diffuse reflectance, N = nitroethane, D = *o*-dichlorobenzene. ^c sh = Shoulder, v = very, br = broad.

presence of a trace of ligand, whereas solutions in other solvents such as 1,2-dichloroethane, chloroform, acetone, and acetonitrile, decompose more rapidly.

A cobalt(II) complex with formula $[\text{Co}(\text{Me}_6\text{tpt})](\text{BPh}_4)_2$ has also been isolated; this is insoluble in all of the above solvents.

Conductometric and spectrophotometric data are reported in Table 2. X-Ray powder patterns of the $[\text{Ni}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ complexes are practically identical to those of $[\text{Co}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ analogues for any given halogen.

$[\text{Ni}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ Complexes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).—These complexes are all of the high-spin type (Table 1). Reflectance spectra for all these compounds are similar to each other: they show four main bands in the ranges 5.7–5.9, 9.1–9.5, 12.7–12.8, and 18.9–20.6 kK (Table 2, Figure 1). Their spectrochemical frequency shift in the order $\text{Cl} > \text{Br} > \text{I}$ is indicative of halide co-ordination.

A comparison with the electronic spectra of corresponding $[\text{Ni}(\text{Me}_6\text{tren})\text{X}]\text{X}$ complexes³ shows that: (i) the two series of spectra exhibit similar features, that is, the same number and shape of absorption maxima; (ii) the whole pattern of bands is shifted to

is evidently distorted from the regular trigonal bipyramidal exhibited by the latter compounds⁴ [points (ii) and (iii)].

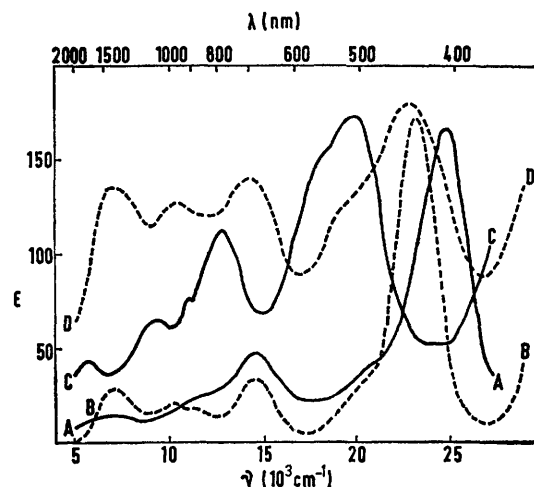
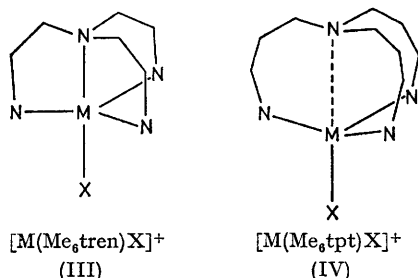


FIGURE 1 Absorption spectra of: $[\text{Ni}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$ (nitroethane soln., curve A); $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (chloroform soln., curve B). Reflectance spectra (arbitrary scale) of: $[\text{Ni}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$ (curve C); $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (curve D)

Molecular models show that in the $[\text{Ni}(\text{Me}_6\text{tpt})\text{X}]^+$ cation (IV), unlike $[\text{Ni}(\text{Me}_6\text{tren})\text{X}]^+$ (III), the greater



length of the aliphatic chain allows the apical nitrogen to be at a greater distance from the metal, thus partially releasing the steric constraints derived from the presence of three six-membered chelate rings.⁵ As it will be shown later, the spectra of the (Me_6tpt) -cobalt(II) complexes clearly indicate a tetrahedral distortion, which can also be suggested for the nickel(II) analogues on the basis of the similarity between X-ray powder patterns of corresponding cobalt(II) and nickel(II) complexes.

The lowering in frequency of the absorption bands in Me_6tpt with respect to Me_6tren complexes is also consistent with the reported ligand-field calculations for a decrease in the ν_{axz}/ν_{eg} ratio.⁶

The complexes behave as 1:1 electrolytes in nitroethane solution (Table 2). Their absorption spectra in this solvent (Table 2, Figure 1) differ to some extent from those in the solid state, but are, nevertheless, very similar both to one another and to those of the analogous $[\text{Ni}(\text{Me}_6\text{tren})\text{X}]\text{X}$ complexes; that is, typical of a regular trigonal bipyramidal structure. Unlike the Me_6tren complexes, whose absorption and reflectance spectra are practically identical, the (Me_6tpt) -nickel(II) complexes have a less 'rigid' structure, which is affected (as shown by the spectral changes) by lattice forces as well as by solute-solvent interactions.

$[\text{Co}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ Complexes (X = Cl, Br, I).— These complexes are of the high-spin type (Table 1). The strong similarity of their X-ray powder patterns with those of the corresponding five-co-ordinate nickel(II) complexes suggests that the co-ordination geometry for the two series of complexes is substantially identical.

The reflectance spectra of $[\text{Co}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ complexes (Figure 2) are notably different from those of $[\text{Co}(\text{Me}_6\text{tren})\text{X}]\text{X}$, being rather similar to those of pseudo-tetrahedral cobalt(II) complexes:⁷ this constitutes good evidence for the suggested tetrahedral distortion in the Me_6tpt complexes (IV). Co-ordination of the halide ion is again supported by the spectrochemical shift of the maxima, as well as by the increased

splitting in the bands at 6.0–8.0 kK in the order $\text{Cl} < \text{Br} < \text{I}$ (Table 2).

A tetrahedral distortion of the suggested type has, in fact, been found by X-ray analysis in the high-spin cobalt(II) complexes with the tripod ligands tris-(2-diphenylphosphinoethyl)amine (NP_3)⁸ and *NN*-bis-(2-diphenylphosphinoethyl)-2-methoxyethylamine (NOP_2).⁹ In these complexes, the Co-N distance is very large (2.4–2.6 Å) and the X-Co-P angle ranges from 104–106°.

The electronic spectra of $[\text{Co}(\text{Me}_6\text{tpt})\text{X}]\text{BPh}_4$ complexes show remarkable changes on passing from the solid state to solutions. In *o*-dichlorobenzene (solvent of low polarity) they exhibit the characteristic features

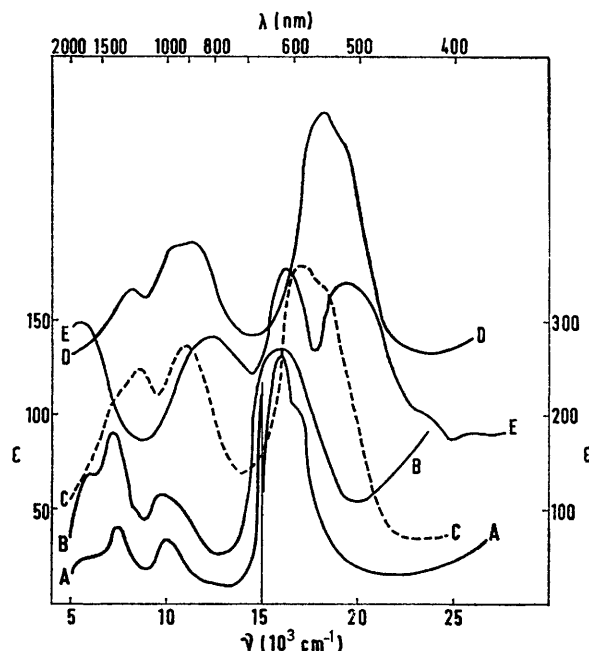


FIGURE 2 Absorption spectrum of *o*-dichlorobenzene solution of $[\text{Co}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$ (curve A). Reflectance spectra (arbitrary scale) of: $[\text{Co}(\text{Me}_4\text{en})\text{Br}_2]$ (curve B); $[\text{Co}(\text{Me}_6\text{tpt})\text{Br}]\text{BPh}_4$ (curve C); $[\text{Co}(\text{Me}_6\text{tpt})](\text{BPh}_4)_2$ (curve D); $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (curve E)

of pseudo-tetrahedral complexes as, for instance, $[\text{Co}(\text{Me}_4\text{en})\text{Br}_2]$ ($\text{Me}_4\text{en} \equiv \text{NNN}'\text{N}'$ -tetramethylethylenediamine)¹⁰ (Figure 2), whereas in nitroethane (solvent of high polarity) a pattern of bands is observed which is not indicative of any definite stereochemistry, thus indicating extensive solvation.¹¹

The conductivity values in nitroethane for the chloro- and bromo-complex are in the range for 1:1 electrolytes (Table 2), whereas the iodo-complex has a notably higher value (120 $\text{cm}^2 \text{ohm}^{-1}$). However conductometric dilution studies¹² have shown that all three

⁵ A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 1968, **7**, 865; A. Vacca and P. Paoletti, *J. Chem. Soc. (A)*, 1968, 2378.

⁶ M. Ciampolini, *Inorg. Chem.*, 1966, **5**, 35.

⁷ R. L. Carlin in 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1966, vol. I.

⁸ L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4465.

⁹ P. Dapporto, G. Fallani, and L. Sacconi, unpublished data.

¹⁰ L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1967, **6**, 262.

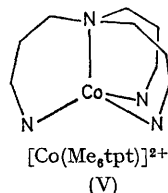
¹¹ Additional experimental data are available and can be had on request from the authors.

¹² See for example R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 1970, **9**, 1215, and references therein.

complexes follow the Onsager law, the slope of $\Lambda_0 - \Lambda_c$ vs. \sqrt{c} plot being in the range for typical 1:1 electrolytes.¹¹

Conductometric and spectrophotometric measurements at different temperatures seem to exclude the existence of temperature-dependent equilibria.¹¹

[Co(Me₆tpt)](BPh₄)₂ Complex.—The reflectance spectrum of this high-spin compound (Figure 2) agrees in its general features with the reported spectra of pseudo-tetrahedral cobalt(II) compounds.^{7,13} This is clearly suggestive of a [Co(Me₆tpt)]²⁺ cation in which the cobalt ion is 'inside' the tetrahedrally bonded ligand (V).



This co-ordinative behaviour is probably favoured by the strong tendency of cobalt(II) toward tetrahedral co-ordination, as well as by the intrinsic structure of the ligand molecule whose trimethylenic chains are long enough to allow full co-ordination of all nitrogen atoms (in absence of a fifth competitive anion X⁻).

Similar results were obtained with the ligand tris-(3-isopropyliminopropyl)amine, whose steric requirements are close to those of Me₆tpt.¹⁴

CONCLUSIONS

It has been reported recently that, (i) cobalt(II) complexes with tris-(3-aminopropyl)amine (tpt)¹⁴ and (ii) nickel(II) and cobalt(II) complexes with tris-(2-diethylaminoethyl)amine (Et₆tren)¹⁵ both maintain essentially the regular trigonal bipyramidal structure found for tren and Me₆tren complexes respectively. In other words, neither lengthening the aliphatic chains, nor increasing the bulkiness of terminal donor groups are sufficient, by themselves, to affect the basic 'rigid' [M(ligand)X]⁺ geometry (ligand = tren, Me₆tren).

The present data indicate that a ligand containing both trimethylenic chains and hindered terminal donor atoms (Me₆tpt) can induce in the complex cation sufficient strain to make it very sensitive to lattice forces, but at the same time is flexible enough to allow a variety of structural alternatives when lattice constraints are released (outside the solid state). Thus a five-co-ordinated structure with a pronounced tetrahedral distortion is observed in the solid complexes, whereas in solution either the five- or four-co-ordinated structure is favoured, depending on the specific tendency of the

metal ion to adopt either stereochemistry. In this case, five-co-ordination is favoured over four-co-ordination in the order Ni > Co; the reverse order was found when the alternative was between five- and six-co-ordination, e.g. in the tren series.^{2a}

Attempts to isolate metal complexes of the more hindered tris-(3-diethylaminopropyl)amine (Et₆tpt) ligand were unsuccessful, which further confirms the critical steric requirements of the Me₆tpt ligand.

EXPERIMENTAL

Synthesis of the Ligand.—Tris-(3-chloropropyl)amine hydrochloride was obtained by treatment of the corresponding alcohol with thionyl chloride; it had m.p. 85–87° (Found: C, 38.2; H, 7.0; Cl, 49.1; N, 4.9. C₉H₁₉Cl₃N requires C, 38.2; H, 6.75; Cl, 50.1; N, 4.90%). A sample (28.5 g., 0.1 mole) of the above compound dissolved in a mixture of ethanol (200 ml) and 33% aqueous dimethylamine (200 ml.) was stirred at 40–50° for 24 hr. and then boiled for 1 hr. to evaporate the excess of dimethylamine; it was then concentrated to small volume under reduced pressure. The amine ligand was freed as an insoluble oil by treatment with an excess of 40% aqueous potassium hydroxide; the mixture was extracted twice with ether. After evaporation of the solvent, the crude ligand was dried (CaSO₄) and fractionally distilled under reduced pressure. The fraction distilling at 125–128°/1 Torr was collected, redistilled, and stored over solid KOH (Found: C, 66.8; H, 14.3; N, 21.3. C₁₅H₃₆N₄ requires C, 66.1; H, 13.3; N, 20.55%).

Preparation of the Complexes.—All the complexes were prepared by the same general method. The use of dry solvents and of dry nitrogen atmosphere throughout was essential because of the high sensitivity of the complexes to moisture. To a solution of the appropriate metal salt (2 mmoles) and the ligand (2 mmoles) in hot butan-1-ol (20 ml.), was added sodium tetraphenylborate (2 mmoles) in the same solvent (10 ml.). The solution was filtered and concentrated by distillation until crystallization occurred. Reaction of Me₆tpt with cobalt(II) thiocyanate under the above conditions gave a purple precipitate of stoichiometric formula corresponding to [Co(Me₆tpt)]-(BPh₄)₂. All the complexes were filtered off on a sintered-glass funnel, washed several times with hot butan-1-ol and light petroleum and dried *in vacuo* at 70°. Attempted recrystallization of the complexes was unsuccessful.

Materials and Physical Measurements.—All solvents were reagent grade. All physical measurements were carried out as described previously.¹⁶

We thank Professor L. Sacconi for his interest and helpful discussions. Thanks are also due to Mr. F. Cecconi and Mr. P. Innocenti for technical assistance, Dr. J. Gelsomini for microanalyses, Mr. F. Nuzzi for the metal analyses, and the Italian C.N.R. for financial support.

[0/2036 Received, December 1st, 1970]

¹³ M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, 1962, **84**, 1543; L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 411.

¹⁴ L. V. Interrante and J. L. Shafer, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 411.

¹⁵ L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1969, 2904.

¹⁶ L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1968, 2997; L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1968, **90**, 5443; L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.