Iron(II), Cobalt(II) and Nickel(II) Complexes with the Tripod Ligand Tris(3,5-dimethyl-1-pyrazolylmethyl)amine.
Ferromagnetic Exchange Coupling in Hexa-coordinated Dimeric Nickel(II) Complexes

F. MANI and G. SCAPACCI

Istituto di Chimica Generale ed Inorganica dell'Università di Firenze, Laboratorio C.N.R., via J. Nardi 41, Florence, Italy

Received May 15, 1979

The new ligand tris(3,5-dimethyl-1-pyrazolyl-methyl)amine (MeTPyA) has been synthesized and its coordinating capacity investigated towards iron(II), cobalt(II), and nickel(II). The complexes have the formulae M(MeTPyA)XBPh₄ (M = Fe, X = Cl, Br; M = Co, X = Cl, Br, I, NCS; M = Ni, X = Cl, Br), Ni(MeTPyA)FBPh₄·acetone, Fe(MeTPyA)-(NCS)₂, and Co(MeTPyA)(NO₃)₂.

The coordination geometries of the complexes are proposed on the basis of spectral, magnetic, conductivity data and X-ray powder photographs. The iron complexes are penta- and hexa-coordinated; the cobalt complexes seem to have coordination geometry intermediate between trigonal-bipyramidal and tetrahedral. The nickel derivatives have a dimeric hexa-coordinated structure with a ferromagnetic exchange coupling between adjacent metal atoms.

Introduction

A number of poly-pyrazolyl derivatives with a variety of metal ions have been reported recently [1]. However examples of such ligands with an apical donor atom appear to be lacking. We have synthesized two new ligands which have a tripodal shape and four potential donor sites, namely tris(1-pyrazolylmethyl)amine and tris(3,5-dimethyl-1-pyrazolyl-methyl) amine.
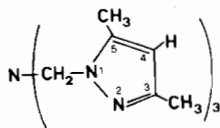
Now we report the synthesis of the latter ligand (hereafter indicated as MeTPyA) and a number of iron(II), cobalt(II), and nickel(II) complexes which have been characterized with the usual methods.

Experimental

Preparation of the Ligand

0.20 mol of $N(CH_2Cl)_3$, prepared from hexamethylenetetramine and PCl_5 as previously described [2], were dissolved in anhydrous THF (100 ml) and slowly dropped into a suspension of potassium 3,5-dimethylpyrazolate, in excess to the stoichiometric ratio, in 400 ml of anhydrous THF. The mixture was refluxed for *ca.* one hour, cooled to room temperature and centrifuged to eliminate KCl. The solution was evaporated on a steam bath until a crude oil was obtained which was separated from the unreacted 3,5-dimethylpyrazole with repeated crystallizations from petroleum ether until the infrared spectrum of the recovered oil did not show the N–H stretching frequency of the 3,5-dimethylpyrazole. The final dense oil was distilled at 175–178 °C (0.3 torr) to yield about 30 g (44%) of MeTPyA as a dense oil which slowly crystallized as white needles. *Anal.* Calcd for $C_{18}H_{27}N_7$: C, 63.31; H, 7.69; N, 28.72. Found: C, 63.1; H, 8.31; N, 28.8. The ¹H NMR spectrum of the ligand was recorded in d-chloroform at 34 °C using TMS as an internal reference. The 4-H and CH_2 proton shifts appear as singlets at δ 5.63 ppm and δ 4.84 ppm respectively. The 3,5-Me_2 proton resonance is a doublet at δ 2.05 ppm and 1.73 ppm. The intensity ratios among the 4-H, CH_2, CH_3 resonance peaks are approximately 1:2:3.

Preparation of the Complexes

The halo-complexes (except the fluoro-derivative) were prepared in absolute ethanol or n-butanol as follows. Warm solutions of stoichiometric amounts of the ligand and $NaBPh_4$ were added to a warm solution of the appropriate anhydrous metal halide. The fluoro-derivative of nickel was prepared as above starting from $Ni(BF_4)_2$. In some cases the solutions were concentrated and allow to cool to room temper-

TABLE I. Analytical Data for the Complexes.

	Found %			Calcd %		
	C	H	N	C	H	N
[Fe(MeTPyA)Cl] BPh$_4$	67.3	6.28	13.0	67.08	6.30	13.04
[Fe(MeTPyA)Br] BPh$_4$	63.4	6.05	11.9	63.34	5.95	12.32
[Fe(MeTPyA)(NCS)$_2$]	46.8	5.29	24.5	46.79	5.30	24.56
[Co(MeTPyA)Cl] BPh$_4$	66.4	6.36	12.4	66.80	6.28	12.99
[Co(MeTPyA)Br] BPh$_4$	62.7	5.98	12.2	63.09	5.93	12.27
[Co(MeTPyA)I] BPh$_4$	59.3	5.85	11.5	59.59	5.60	11.59
[Co(MeTPyA)NCS] BPh$_4$	66.6	6.49	14.6	66.41	6.09	14.41
[Co(MeTPyA)NO$_3$] NO$_3$	40.9	5.58	23.6	41.23	5.19	24.05
[Ni(MeTPyA)F] BPh$_4$·(CH$_3$)$_2$CO[a]	67.7	7.03	12.2	67.86	6.70	12.32
[Ni$_2$(MeTPyA)$_2$Cl$_2$] (BPh$_4$)$_2$[b]	66.7	6.49	13.0	66.82	6.28	12.99
[Ni$_2$(MeTPyA)$_2$Br$_2$] (BPh$_4$)$_2$[c]	62.8	6.16	12.1	63.11	5.93	12.27

[a]Ni: found 7.25, calcd 7.71.   [b]Cl: found 4.65, calcd 4.70.   [c]Br: found 10.3, calcd 9.99.

TABLE II. Some Physical Data for the Complexes.

	μ_{eff}, μ_B[a] (298 K) (88 K)		Λ_M[b], S cm^2 mol^{-1}	State[c]	Electronic Spectra, μm^{-1} (ϵ_{molar} for soln in parentheses)
[Fe(MeTPyA)Cl] BPh$_4$	5.50	5.73	103	R	1.0
				A	0.54(68), 0.90(30)
[Fe(MeTPyA)Br] BPh$_4$	5.11		113	R	0.53, 0.83
				A	0.54(69), 0.87(27)
[Fe(MeTPya)(NCS)$_2$]	5.31		21	R	1.1
				A	1.0(25)
[Co(Me(TPyA)Cl] BPh$_4$[d]	4.21		99	R	0.60sh, 0.69, 1.16, 1.82
				A	0.61(74), 0.71(76), 1.17(57), 1.68(315), 1.98(234)
[Co(Me(TPyA)Br] BPh$_4$[e]	4.35		98	R	0.59sh, 0.69, 1.15, 1.82
				A	0.59, 0.71(95), 1.15(49), 1.71(405), 1.87(248)
[Co(MeTPyA)I] BPh$_4$	4.36		103	R	0.59sh, 0.68, 1.16, 1.74
				A	0.60, 0.70(123), 1.13(66), 1.70(553), 1.89
[Co(MeTPyA)NCS] BPh$_4$	4.27		999	R	0.53sh, 0.67, 1.33, 1.80, 2.00 sh
				A	0.54, 0.72(165), 1.31(55), 1.74(655), 2.00(220)
[Co(MeTPyA)NO$_3$] NO$_3$	4.28		90	R	0.75, 1.15, 1.48, 1.94
				A	0.77(36), 1.10, 1.43(33), 20.0(157)
[Ni(MeTPya)F] BPh$_4$·(CH$_3$)$_2$CO	3.15	3.28	88	R	0.95, 1.60, >2.5
				A	0.97(20), 1.64(13), >2.5
[Ni$_2$(MeTPyA)$_2$Cl$_2$] (BPh$_4$)$_2$[f]	3.15	3.34	196	R	0.95, 1.55, 2.50
				A	0.93(18), 1.55(20), 2.50(32)
[Ni$_2$(MeTPyA)$_2$Br$_2$] (BPh$_4$)$_2$[g]	3.20	3.37	194	R	0.89, 1.48, 2.50
				A	0.91(16), 1.50(22), 2.45(35)

[a]1 μ_B = 9.27 × 10^{-24} A m^2. The values are per metal atom.   [b]For ca. 10^{-3} M solutions in acetone; S = kg^{-1} m^{-2} s^3 A^2 = Ω^{-1}.
[c]R = diffuse reflectance; A = acetone soln. $(\Lambda_o - \Lambda_e)/\sqrt{c}$ values: d, 500; e, 485; f, 750; g, 690.

ature to effect crystallization. The thiocyanate–tetraphenylborate cobalt complex was prepared as above using Co(NCS)$_2$. Iron(II) dithiocyanate and cobalt(II) dinitrate were used for the preparation of the corresponding complexes. All of the complexes with the exception of [Fe(MeTPyA)X] BPh$_4$ (X = Cl, Br) were recrystallized from a CH$_2$Cl$_2$-n-butanol solution.

The iron(II) complexes were prepared in a dry nitrogen atmosphere using degassed solvents.

Physical Measurements

The apparatus and experimental techniques used for the magnetic measurements and electronic spectra are described in previous papers [3]. The conductivity data were measured on a WTW Model LBR/B

conductance bridge. Concentration of the solutions in acetone ranges approximately between 10^{-4} and 5×10^{-3} M. The reference values for *ca.* 10^{-3} M solutions of a series of tetraalkylammonium halides are *ca.* 100–150 S cm^2 mol^{-1} [4]. X-ray powder photographs have been made with a Philips model PW 1130 X-ray generator using an iron anticathode and manganese as a filter. Infrared spectra were obtained with a Perkin-Elmer model 283 grating spectrophotometer. The samples were prepared as Nujol mulls and KBr discs. Proton magnetic resonance spectra were recorded on a Varian EM 390 spectrometer at 90 MHz. Shifts were calibrated from internal tetramethylsilane. Deuteriochloroform was used as solvent.

Results and Discussion

Iron(II) Complexes

The complexes have formulae [Fe(MeTPyA)X]·BPh$_4$ (X = Cl, Br) and [Fe(MeTPyA)(NCS)$_2$]. These complexes are of the high-spin type with four unpaired electrons (Table II). The electronic spectrum of dithiocyanate derivative both in the solid state and in solution as well as its stoichiometry clearly indicate a hexa-coordinate geometry. Moreover the infrared spectrum in ν(CN) region with a strong absorption at 2065 cm^{-1} is indicative of terminal thiocyanate N-bonded. A *cis*-octahedral geometry is assigned to the dithiocyanate complex on account of the shape when the ligand is a tetradentate. The chloro-derivative is also assigned a hexa-coordinated structure in the solid state on the basis of spectral evidences. A dimeric or polymeric structure involving two chlorine bridges is consistent with the proposed hexa-coordinated structure and with the stoichiometry of the complex. Interestingly, this bridging structure leads to a slight ferromagnetic exchange.

The absorption spectrum in acetone of [Fe(MeTPyA)Cl]BPh$_4$, where the complex is 1:1 electrolyte, bears no relation to the solid reflectance spectrum and correlates well with the spectra of penta-coordinated trigonal bipyramidal iron(II) complexes having the same N$_4$X donor set, as particularly exemplified by [Fe(Me$_6$tren)X]$^+$ (Me$_6$tren is tris(dimethylamine-ethyl)amine) [5]. The bromo-derivative too is assigned a penta-coordinated trigonal bipyramidal geometry on the basis of its electronic spectra both in the solid state and in solution, as well as of its molar conductivity in acetone.

Cobalt(II) Complexes

The complexes have formulae [Co(MeTPyA)X]·BPh$_4$ (X = Cl, Br, I, NCS) and are of the high-spin type. They are easily soluble in acetone where behave as 1:1 electrolytes.

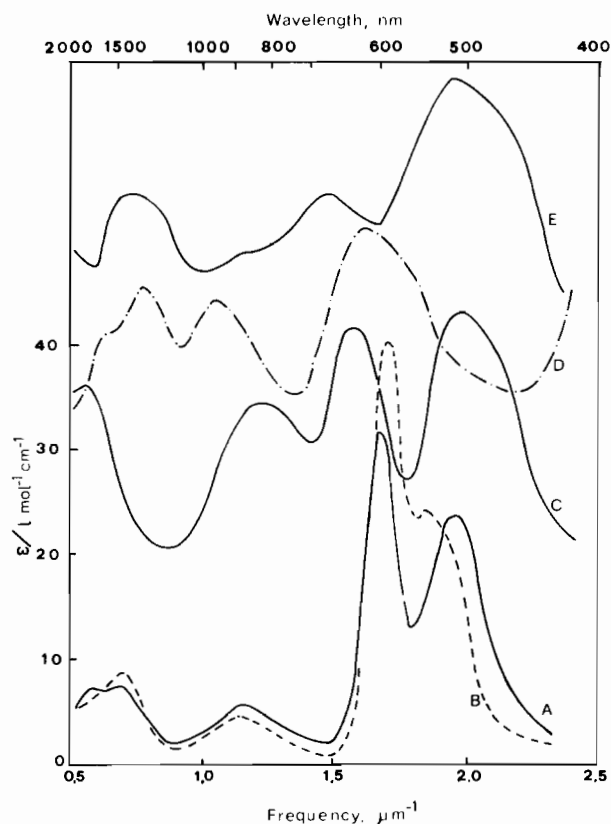Fig. 1. Absorption spectra in acetone of: A, [Co(MeTPyA)-Cl]BPh$_4$; B, [Co(MeTPyA)Br]BPh$_4$; reflectance spectra of: C, [Co(Me$_6$tren)Cl]Cl; D, [Co(Me$_3$tn)Cl$_2$]; E, [Co(MeTPyA)NO$_3$]NO$_3$.

The close similarity of the infrared spectra and X-ray powder photographs between [Fe(MeTPyA)-Br]BPh$_4$ and [Co(MeTPyA)X]BPh$_4$ suggests that the coordination geometry is similar in iron and cobalt complexes. Nevertheless the electronic spectra of the cobalt complexes (Fig. 1) are significantly different from those of the trigonal bipyramidal [Co(Me$_6$-tren)X]$^+$ [6] being rather similar to those of pseudo-tetrahedral cobalt(II) complexes [7]. Both spectral and diffractometric features of the [Co(MeTPyA)X]·BPh$_4$ derivatives can be reconciled by assuming a trigonal bipyramidal structure severely distorted towards a tetrahedron, with the apical nitrogen atom which can be considered 'semi-coordinated'. As a matter of fact X-ray structural analysis of a number of supposed penta-coordinated high-spin cobalt(II) complexes with tetradentate tripodal ligands [8] has revealed that the complexes actually have structures intermediate between a trigonal bipyramid and a tetrahedron as the apical nitrogen atom lies at a markedly longer distance from the metal as compared to the remaining four donors.

The [Co(MeTPyA)(NO$_3$)]NO$_3$ complex is a 1:1 electrolyte in acetone solution. The electronic spectra

both in the solid state and in solution show four bands (Fig. 1) shifted to higher energies in respect to those of the halo-complexes and compare favourably with those of known distorted penta-coordinated complexes as, for instance, [Co(nop$_2$)X]BF$_4$ [7b] (nop$_2$ is N,N-bis-(2-diphenylphosphinoethyl)-2-methoxyethylamine). Moreover the infrared spectrum recorded in KBr discs shows two bands at 1283, 1490 cm^{-1} which can be tentatively assigned as N—O stretch frequencies of bidentate NO$_3$ and a band at 1380 cm^{-1} attributable to ionic NO$_3$ [9]. Two bands at 810 and 823 cm^{-1} can be assigned as out-of-plane def. of bidentate NO$_3$ and ionic NO$_3$ respectively. On this basis a distorted penta-coordinated structure can be assigned to the dinitrate complex with the tridentate ligand MeTPyA and bidentate NO$_3$.

Nickel(II) Complexes

The diffuse reflectance spectra and the absorption spectra of the complexes Ni(MeTPyA)XBPh$_4$ (X = Cl, Br) and Ni(MeTPyA)FBPh$_4$·acetone, with three bands at ca. 0.9, 1.5, and 2.5 μm^{-1}, are easy to assign on the basis of an octahedral symmetry. On account of their stoichiometry it is conceivable that the hexa-coordination in the nickel complexes is attained through halide bridges. The X-ray powder patterns as well as the infrared spectra of the chloro- and bromo-derivative are quite similar to each other; the fluoro-derivative has an infrared spectrum similar to those of the previously reported halo-complexes (apart the band at 1710 cm^{-1} due to the free acetone) but a rather different X-ray powder photograph.

Conductometric dilution studies [10] in acetone have been performed for Ni(MeTPyA)XBPh$_4$ and for Co(MeTPyA)XBPh$_4$ for comparison purposes. The chloro- and bromo-derivatives follow the Onsager law, the slope of $\Lambda_o - \Lambda_e$ vs. $\sqrt{C_M}$ being in the range 700–750 for nickel complexes and 480–500 for cobalt complexes. The values found for nickel complexes, as compared with values in the range 500–540 for the 1:1 electrolyte But$_4$NBPh$_4$ and with those of cobalt complexes, seem to indicate 2:1 electrolytes (X = Cl, Br) and consequently the dimeric formulae [Ni$_2$(MeTPyA)$_2$X$_2$](BPh$_4$)$_2$. No conclusion can be drawn about the structure of the fluoro-derivative as this compound does not strictly follow the Onsager law and is not isomorphous with the other halo-complexes.

The magnetic moment values of all the three halo-complexes are in the range 3.15–3.20 μ_B at 298 K. As the temperature is decreased, μ_{eff} of the complexes gradually increases until the values of 3.28–3.37 μ_B are reached at 88 K (Table II). Moreover the room temperature magnetic moment of [Ni$_2$(MeTPyA)$_2$Br$_2$](BPh$_4$)$_2$ is field-dependent being 3.20 μ_B at 0.93 T and 2.39 μ_B at 0.62 T (1 tesla is equivalent to 10^4 gauss). On the contrary no field-dependence of the susceptibility could be detected for the chloro and fluoro analogues in the temperature range investigated. The temperature dependence of the magnetic moments as well as the field-strength dependence in the case of the bromo-derivative, strongly suggest the existence of intramolecular ferromagnetic interactions between adjacent nickel atoms through bridging halides [11].

The decomposition of M(BF$_4$)$_2$ salts, assisted by strongly basic and sterically hindred ligands, and the formation of fluoro-complexes has been now well ascertained [12]. However only recently examples of complexes with bridging fluorine atoms have been reported [12a]. Moreover the [Ni(MeTPyA)F]BPh$_4$·acetone is the only example of ferromagnetic exchange coupling between metal ions linked by fluorine bridges.

Conclusions

The MeTPyA ligand can form complexes with different coordination numbers, six, five and intermediate between four and five, and different coordination geometries, acting as tetra- and tridentate or being intermediate between tetra- and tridentate. These results show that the ligand molecule possesses a sufficient flexibility to allow the metals to dictate the preferred coordination number and geometry, in spite of the tripodal tetradentate nature of the ligand.

Thus the coordination geometry of the cobalt complexes, intermediate between a trigonal bipyramid and a tetrahedron, originates from the well known tendency of cobalt(II) towards tetrahedral coordination, owing to the stability of the $e^4t_2^3$ configuration for d^7 electrons in T$_d$ ligand field.

References

1 S. Trofimenko, *Chem. Rev.*, *72*, 498 (1972); K. R. Breakell, D. J. Patmore, and A. Storr, *J. Chem. Soc. Dalton*, 749 (1975); P. Dapporto, F. Mani, and C. Mealli, *Inorg. Chem.*, *17*, 1323 (1978); F. Mani and R. Morassi, *Inorg. Chim. Acta*, *36*, 63 (1979).
2 E. Fuck and P. Meiser, *Chem. Bzr.*, *106*, 69 (1973).
3 L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, *82*, 3487 (1960); L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, *7.*, 1417 (1968).
4 W. J. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).

5 M. Ciampolini and N. Nardi, *Inorg. Chem.*, *5*, 1150 (1966); M. di Vaira and P. L. Orioli, *Acta Cryst.*, *B24*, 1269 (1968).

6 M. Ciampolini and N. Nardi, *Inorg. Chem.*, *5*, 41 (1966).

7 a) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, *6*, 262 (1967); b) L. Sacconi and R. Morassi, *J. Chem. Soc.*, *492* (1971).

8 L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, *90*, 5443 (1968).

9 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, *4*, 804 (1965).
M. di Vaira and A. Bianchi Orlandini, *Inorg. Chem.*, *12*, 1292 (1973); M. di Vaira, *J. Chem. Soc. Dalton*, 1575 (1975).

10 R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

11 K. O. Young, C. J. O'Connor, E. Sinn, and R. L. Carlin, *Inorg. Chem.*, *18*, 804 (1979); A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, *11*, 2884 (1972); J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, *10*, 240 (1971); A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, *7*, 932 (1968).

12 a) J. Reedijk, J. C. Jansen, H. van Koningsveld and C. G. van Kralingen, *Inorg. Chem.*, *17*, 1990 (1978); M. A. Guichelar, J. A. M. van Hest, and J. Reedijk, *Inorg. Nucl. Chem. Letters*, 10, 999 (1974); P. Dapporto and F. Mani, submitted for publication.