

# Synthesis and Structural Study of Cobalt(II) Complexes with the Polypyrazolyl Ligand Tris(1-pyrazolyylethyl)amine, TPyEA.

## Crystal and Molecular Structure Determination of the Dinuclear Complex $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$

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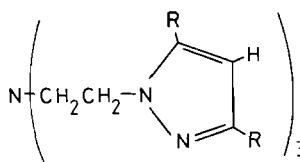
Received July 3, 1982

Cobalt(II) complexes with the tetradentate ligand tris(1-pyrazolyylethyl)amine, TPyEA, and a variety of co-ligands have been synthesized and characterized. The complexes with general formula  $[\text{CoX}(\text{TPyEA})]\text{-BPh}_4$  are mononuclear and five-coordinate when  $X = \text{NCS}$ ,  $\text{NCO}$ ,  $\text{I}$ ,  $\text{ClO}_4$ , or dinuclear with six-coordinate metal centers when  $X = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{N}_3$ . The structure of the dinuclear bromo derivative has been determined by X-ray analysis. Each cobalt atom in the dinuclear  $[\text{CoBr}(\text{TPyEA})]_2^{2+}$  cation is coordinated by the four nitrogen donor atoms of the TPyEA ligand and by the two bridging bromine atoms in a distorted octahedral geometry. The dinuclear complexes are reversibly converted in the solid state to mononuclear five-coordinate species by heating or grinding. The same dissociation occurs upon dissolution in acetone. The complexes with bidentate co-ligands,  $[\text{CoY}(\text{TPyEA})]\text{BPh}_4$  ( $Y = 2$ -mercaptobenzoate),  $[\text{CoY}(\text{TPyEA})]\text{ClO}_4$  ( $Y = \text{acetylacetonate}$ ,  $\text{benzoylacetate}$ ), and  $[\text{Co}(\text{NCS})_2(\text{TPyEA})]$  are six-coordinate. Also the above six-coordinate bis thiocyanate complex undergoes a transformation upon dissolution or grinding.

### Introduction

During the last few years a systematic research in this laboratory has been directed to the synthesis and characterization of 3d metal complexes of polydentate ligands containing pyrazole donor groups [1]. Recently it has been reported that the tetradentate ligand tris(3,5-dimethyl-1-pyrazolyylethyl)amine, MeTPyEA, forms four-coordinate complexes  $[\text{Co}(\text{MeTPyEA})]^{2+}$  with unusual structural and spectral properties [2]. Consequently, we decided to synthesize the unmethylated ligand tris(1-pyrazolyylethyl)amine, TPyEA, and its cobalt complexes in order to investigate the effects on coordination

due to the reduced steric hindrance on going from the methylated to the unmethylated ligand.



$R = \text{H}$ , TPyEA

$R = \text{CH}_3$ , MeTPyEA

Cobalt(II) complexes formed by ligands of this type are of interest as they may serve as active site approximations for metalloenzymes and metalloproteins [3].

In this paper we report on the synthesis and characterization and on some peculiar properties of the complexes having the general formula  $[\text{CoX}(\text{TPyEA})]\text{BPh}_4$  ( $X = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NCS}$ ,  $\text{NCO}$ ,  $\text{N}_3$ ,  $\text{ClO}_4$ , 2-mercaptobenzoate),  $[\text{CoF}(\text{TPyEA})]\text{BF}_4$ ,  $[\text{Co}(\text{NCS})_2(\text{TPyEA})]$ , and  $[\text{CoY}(\text{TPyEA})]\text{ClO}_4$  ( $Y = \text{acetylacetonate}$ ,  $\text{benzoylacetate}$ ).

In order to achieve a better understanding of the properties of the above complexes, the structure of the compound  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$  has been investigated by X-ray diffraction methods.

### Experimental

#### Syntheses of the Ligand and of the Complexes

The ligand TPyEA was prepared starting from  $\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_3$  [4] and potassium pyrazolate by a procedure similar to that already described for the synthesis of the methylated MeTPyEA ligand [5]. The final product obtained as a viscous oil was distilled at 196–198 °C and 2 mmHg. *Anal.* Calcd for

TABLE I. Analytical Data for the Complexes.

	Found %			Calcd %		
	C	H	N	C	H	N
[CoF(TPyEA)]BF <sub>4</sub>	39.4	5.27	21.0	38.81	4.56	21.12
[CoF(TPyEA)]BPh <sub>4</sub>	67.7	6.48	13.4	67.25	5.93	14.08
[CoCl(TPyEA)]BPh <sub>4</sub>	65.4	5.93	14.1	65.70	5.80	13.75
[CoBr(TPyEA)]BPh <sub>4</sub> <sup>a</sup>	63.4	5.57	13.1	61.84	5.46	12.94
[CoI(TPyEA)]BPh <sub>4</sub>	57.7	5.26	12.4	58.23	5.14	12.19
[Co(NCS)(TPyEA)]BPh <sub>4</sub>	65.5	5.80	15.9	65.31	5.62	15.23
[Co(NCO)(TPyEA)]BPh <sub>4</sub>	66.1	5.82	15.4	66.77	5.74	15.57
[Co(N <sub>3</sub> )(TPyEA)]BPh <sub>4</sub>	64.6	5.84	20.0	65.10	5.74	19.47
[Co(ClO <sub>4</sub> )(TPyEA)]BPh <sub>4</sub> <sup>b</sup>	59.8	5.70	12.3	60.28	5.32	12.62
[Co(acac)(TPyEA)]ClO <sub>4</sub> <sup>d</sup>	43.4	5.29	17.7	43.14	5.07	17.61
[Co(bzac)(TPyEA)]ClO <sub>4</sub> <sup>d</sup>	48.5	5.01	16.1	48.52	4.88	15.83
[Co(thbz)(TPyEA)]BPh <sub>4</sub> <sup>c,d</sup>	66.3	5.86	11.6	66.51	5.58	11.80
[Co(NCS) <sub>2</sub> (TPyEA)]	43.2	4.73	27.1	43.03	4.46	26.57

<sup>a</sup>Br: found 10.2; calcd. 10.55. <sup>b</sup>Cl: found 4.40; calcd. 4.56. <sup>c</sup>S: found 3.70; calcd 3.86. <sup>d</sup>acac, bzac, thbz stand, respectively, for acetylacetonate, benzoylacetonate, 2-mercaptobenzoate.

C<sub>15</sub>H<sub>21</sub>N<sub>7</sub>: C, 60.18; H, 7.07; N, 32.75. Found: C, 60.4; H, 7.15; N, 33.1%.

The [CoX(TPyEA)]BPh<sub>4</sub> (X = Cl, Br, I, NCS, ClO<sub>4</sub>) complexes were prepared as follows. 10<sup>-3</sup> mol of the ligand in 15 cm<sup>3</sup> of acetone and subsequently 10<sup>-3</sup> mol of NaBPh<sub>4</sub> in 10 cm<sup>3</sup> of ethanol were added to 10<sup>-3</sup> mol of the appropriate hydrated CoX<sub>2</sub> salt dissolved in 25 cm<sup>3</sup> of boiling ethanol. In some cases the solutions were concentrated by boiling until crystallization occurred. The [Co(NCS)<sub>2</sub>(TPyEA)] complex was obtained as above except that NaBPh<sub>4</sub> was not added. The [CoF(TPyEA)]BF<sub>4</sub> derivative was obtained starting from Co(BF<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>. The [CoF(TPyEA)]BPh<sub>4</sub> complex was obtained by adding a solution of NaBPh<sub>4</sub> in ethanol to the mother liquor of the tetrafluoroborate derivative. The complexes [CoX(TPyEA)]BPh<sub>4</sub> (X = NCO, N<sub>3</sub>, 2-mercaptobenzoate) and [CoY(TPyEA)]ClO<sub>4</sub> (Y = acetylacetonate, benzoylacetonate) were prepared starting from a solution of [Co(ClO<sub>4</sub>)(TPyEA)]BPh<sub>4</sub> to which the appropriate reactants (acetylacetonate, benzoylacetonate, 2-mercaptobenzoic acid, KNCO and NaN<sub>3</sub>) were added in excess to the stoichiometric ratio, and by refluxing for several hours. The reaction mixture was then filtered and concentrated to a small volume. In some cases diethyl ether was added to promote crystallization. The complex with 2-mercaptobenzoic acid was prepared under an inert atmosphere. Recrystallization of the products from acetone—absolute ethanol or acetone—diethyl ether led to compounds with satisfactory analyses (Table I).

#### Physical Measurements

Magnetic, spectrophotometric, infrared and conductivity measurements were performed with apparatus and procedures already described [6].

The [CoX(TPyEA)]BPh<sub>4</sub> (X = F, Cl, Br, N<sub>3</sub>) complexes are pink to magenta at room temperature but gradually and reversibly change to a violet colour by heating at temperatures greater than 270 °C (fluoro and chloro derivatives), 240 °C (bromo derivative), and 140 °C (azido derivative). Apparently the same transformation occurs if the chloro and bromo derivatives are subjected to pressure by grinding at room temperature. In the latter two cases the compounds remain in the violet form as long as the temperature is not increased, but they revert to the original pink or magenta colour after heating. Finally, the pink [Co(NCS)<sub>2</sub>(TPyEA)] complex changes to a blue compound by grinding; the same pink complex melts at 186–187 °C in a blue liquid. Magnetic, conductivity and spectral data for the compounds are reported in Table II. Characteristic vibrational frequencies for some of the complexes are: [Co(NCS)(TPyEA)]BPh<sub>4</sub>,  $\nu(\text{CN})$  2082(s); [Co(NCS)<sub>2</sub>(TPyEA)],  $\nu(\text{CN})$  2075(s), 2085(sh); [Co(N<sub>3</sub>)(TPyEA)]BPh<sub>4</sub>,  $\nu(\text{NNN})$  2082(s); [Co(NCO)(TPyEA)]BPh<sub>4</sub>,  $\nu(\text{NCO})$  2210(s). [Co(acac)(TPyEA)]ClO<sub>4</sub>, combined  $\nu(\text{CO}) + \nu(\text{CC})$  1592(s), 1515(s);  $\nu(\text{ClO}_4)$  1100(s, br); [Co(bzac)(TPyEA)]ClO<sub>4</sub>, combined  $\nu(\text{CO}) + \nu(\text{CC})$  1597(s), 1570(s), 1510(s);  $\nu(\text{ClO}_4)$  1090(s, br); [Co(ClO<sub>4</sub>)(TPyEA)]BPh<sub>4</sub>,  $\nu(\text{ClO}_4)$  1120–1143(s), 1075–1080(s), 1035–1040(s); [Co(thbz)(TPyEA)]BPh<sub>4</sub>,

TABLE II. Some Physical Data for the Complexes.

Complex	Colour	$\mu_{\text{eff.}}$ , $\mu_B^a$	$\Delta M^b$ , $2 S \text{ cm}^2 \text{ mol}^{-1}$	State <sup>c</sup>	Abs. max., nm ( $\epsilon_{\text{molar}}$ for soln. in parentheses)
		(298 K)			
[CoF(TPyEA)]BF <sub>4</sub> <sup>d</sup>	pink	4.75		R	460, 490, 520sh, 1075
[CoF(TPyEA)]BPh <sub>4</sub> <sup>d</sup>	pink	4.82	4.53	R	460sh, 490, 520sh, 1090
[CoCl(TPyEA)]BPh <sub>4</sub> <sup>d</sup>	magenta	4.75	4.80	D	490(8), 1050(21)
[CoCl(TPyEA)]BPh <sub>4</sub>	violet	4.68	4.70	R	500, 520sh, 565, 1025sh, 1175
[CoBr(TPyEA)]BPh <sub>4</sub> <sup>d</sup>	magenta	4.83	4.90	A	560(416), 865(56), 1800(64)
[CoBr(TPyEA)]BPh <sub>4</sub>	violet	4.48	4.52	R	560, 865, 1725
[CoI(TPyEA)]BPh <sub>4</sub>	blue	4.40		A	560(440), 865(60), 1830(75)
[Co(NCS)(TPyEA)]BPh <sub>4</sub>	violet	4.39		R	460sh, 500, 525sh, 580, 1025, 1250
[Co(NCO)(TPyEA)]BPh <sub>4</sub>	violet	4.50		A	450sh, 575(250), 880(25), 1800(31)
[Co(N <sub>3</sub> )(TPyEA)]BPh <sub>4</sub> <sup>d</sup>	pink	4.70	4.13	R	575, 880, 1750
[Co(ClO <sub>4</sub> )(TPyEA)]BPh <sub>4</sub>	violet	4.60		A	575(286), 880(35), 1850(46)
[Co(acac)(TPyEA)]ClO <sub>4</sub>	orange	4.67		R	<400, 565, 900, 1750
[Co(bzac)(TPyEA)]ClO <sub>4</sub>	orange	4.71		A	<400, 580(512), 910(46), 1825(71)
[Co(thbz)(TPyEA)]BPh <sub>4</sub>	pink	4.64		R	500, 555, 710, 1700
[Co(NCS) <sub>2</sub> (TPyEA)]	pink	4.72		A	500sh, 555(217), 720(37), 1800(56)
[Co(NCS) <sub>2</sub> (TPyEA)]	blue	4.65		R	545, 745, 1675

<sup>a</sup>  $\mu_B = 9.27 \times 10^{-24} \text{ A m}^2$ . <sup>b</sup> For ca.  $10^{-3} \text{ mol dm}^{-3}$  solutions in the same solvent as the corresponding electronic spectra; reference values are quoted in ref. 7. <sup>c</sup> R = diffuse reflectance; D = dimethylformamide; A = acetone. <sup>d</sup> Minimal formula reported for dinuclear compounds (see text).

TABLE III. Positional Parameters and Anisotropic Temperature Factors for  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$ .<sup>a</sup>

Atom	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	910(2)	954(2)	1490(2)	49(2)	29(2)	38(2)	15(2)	-9(1)	5(1)
Br	509(2)	1291(2)	-573(2)	59(2)	32(1)	42(1)	9(1)	-12(1)	6(1)
N1	1973(13)	2855(12)	2319(13)	67(13)	48(11)	57(12)	34(10)	4(10)	-5(9)
N2	2294(12)	766(13)	869(12)	43(11)	43(10)	54(11)	12(9)	-9(8)	9(8)
N3	1111(12)	392(12)	3000(12)	76(12)	30(9)	37(10)	18(8)	-34(9)	6(8)
N4	-367(12)	1302(12)	2124(12)	67(12)	29(9)	46(10)	23(9)	-6(9)	4(8)
N5	3206(14)	1603(14)	601(15)	60(13)	41(11)	95(14)	16(10)	0(11)	1(10)
N6	1517(18)	1087(15)	4050(15)	187(23)	33(11)	52(13)	19(12)	-51(13)	-5(10)
N7	-466(13)	2333(14)	2236(13)	55(12)	61(12)	55(11)	34(10)	17(9)	11(9)

<sup>a</sup>The form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ ; coordinates multiplied by  $10^4$ , temperature factors by  $10^3$ ; estimated standard deviations on the last significant digits are in parentheses; only parameters for symmetry-independent atoms in the dimeric species are listed.

$\nu(\text{COO})$  1507(s), 1595(m);  $\nu(\text{SH})$  2440(w,br). All the values are in  $\text{cm}^{-1}$ ; s = strong; m = medium; w = weak; br = broad; sh = shoulder.

#### Crystal and Intensity Data

Di- $\mu$ -bromo-bis{tris(1-pyrazolylethyl)aminocobalt(II)}di-tetraphenylborate,  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$ ,  $\text{C}_{78}\text{H}_{82}\text{B}_2\text{Br}_2\text{Co}_2\text{N}_{14}$ , M.W. = 1514.92, triclinic,  $a = 13.549(5)$ ,  $b = 12.846(4)$ ,  $c = 11.772(5)$  Å,  $\alpha = 101.28(5)$ ,  $\beta = 90.01(5)$ ,  $\gamma = 114.28(5)^\circ$ ,  $V = 1824.1$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.379$  g  $\text{cm}^{-3}$ ,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å,  $\mu(\text{MoK}\alpha) = 15.9$   $\text{cm}^{-1}$ , space group  $\text{P}\bar{1}$ .

Crystals of the compound corresponding to the above formula were obtained in form of elongated platelets from an acetone–absolute ethanol solution. A crystal of dimensions *ca.*  $0.50 \times 0.08 \times 0.20$  mm was used for all operations. Intensity data were recorded on a Philips PW 1100 automated diffractometer using graphite monochromated  $\text{MoK}\alpha$  radiation. Unit cell dimensions were determined from the angular measurements of 24 strong reflections in the range  $25\text{--}30^\circ$  in  $2\theta$ . Intensity data were collected in the range  $5 < 2\theta < 46^\circ$  by the  $\theta\text{--}2\theta$  scan technique, with a symmetric scan range of  $0.8 + 0.30\tan\theta$  and a scan speed of  $4.0^\circ/\text{min}$  in  $2\theta$ . Background counts were measured at each end of the scan for a time equal to half the scan time. The intensities of three reflections, monitored periodically throughout data collection, showed only random variations (*ca.* 2%) from the mean values. Corrections for Lorentz and polarization effects were applied. A total of 1991 independent reflections having  $I > 3\sigma(I)$  were used in the solution and refinement of the structure.

#### Solution and Refinement of the Structure

The structure was solved by heavy atom procedures and refined by full-matrix least squares in which the function  $\sum w(|F_o| - |F_c|)^2$  was minimized,

with weights  $w = 1/\sigma^2(F_o)$ . Atoms heavier than carbon were assigned anisotropic temperature factors whereas the C and B atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å), each with a temperature factor *ca.* 20% larger than that of the respective carbon atom. Refinement converged to the conventional  $R$  value of 0.077 ( $R_w = 0.076$ ). Discrepancy indices are defined as  $R = \sum |F_o| - |F_c| / \sum |F_o|$ , and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . The final  $\Delta F$  Fourier showed few peaks, lower than  $0.8 \text{ e}\text{\AA}^{-3}$ , in the proximity of the metal or donor atoms positions. Such features of the  $\Delta F$  map and the spread in values of chemically equivalent bond distances and angles in the ligand molecule, are indicative of a small amount of disorder in the structure. This may be related to the tendency of the compound to undergo reversible transformations in the solid state.

All atomic scattering factors and the anomalous dispersion terms for cobalt were taken from [8]. Calculations were carried out with the programs listed in [9]. Fractional coordinates and temperature factors of the nonhydrogen atoms are listed in Tables III and IV. Important bond distances and angles within the cation appear in Table V. A Table of the observed and calculated structure factors is available on request.

#### Results and Discussion

All of the complexes are high-spin (Table II). The complexes having the general formula  $[\text{CoX}(\text{TPyEA})]\text{BPh}_4$  may be classified in two groups depending on the structures they are assigned, both in the solid state and in solution.

TABLE IV. Positional Parameters and Isotropic Temperature Factors for  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$ .<sup>a</sup>

Atom	X	Y	Z	U (Å <sup>2</sup> )
C1	2856(20)	3342(21)	1601(21)	93(8)
C2	3542(22)	2854(24)	1210(24)	124(10)
C3	2513(18)	2934(19)	3492(19)	80(7)
C4	1747(19)	2324(19)	4261(20)	89(8)
C5	1449(17)	3693(19)	2522(19)	81(7)
C6	357(17)	3263(18)	1852(18)	72(6)
C7	3798(18)	1166(18)	-36(17)	57(6)
C8	3269(16)	-14(18)	-207(17)	66(6)
C9	2359(16)	-228(19)	360(16)	55(6)
C10	1419(24)	427(30)	4829(36)	139(12)
C11	1140(23)	-752(27)	4300(26)	125(10)
C12	973(17)	-646(21)	3166(21)	74(7)
C13	-1318(18)	2290(20)	2770(18)	68(6)
C14	-1881(20)	1249(19)	3003(19)	76(7)
C15	-1225(16)	635(19)	2597(16)	56(6)
C16	6646(15)	3422(15)	3034(15)	44(5)
C17	6867(18)	3589(20)	4250(19)	73(7)
C18	6399(19)	2685(21)	4853(23)	83(7)
C19	5665(22)	1651(25)	4267(24)	99(8)
C20	5341(23)	1412(26)	3118(24)	102(9)
C21	5872(17)	2334(19)	2508(21)	76(7)
C22	6814(14)	3932(14)	926(14)	39(5)
C23	6163(14)	4274(15)	257(15)	45(5)
C24	5870(16)	3798(16)	-916(17)	57(6)
C25	6182(16)	2956(17)	-1495(17)	61(6)
C26	6850(15)	2602(17)	-878(16)	57(6)
C27	7166(15)	3121(15)	299(16)	55(6)
C28	8558(14)	5146(14)	2525(15)	40(5)
C29	9181(16)	5492(15)	1589(17)	52(5)
C30	10330(17)	6114(17)	1706(19)	66(6)
C31	10875(19)	6371(17)	2771(17)	64(6)
C32	10325(17)	6075(16)	3704(19)	61(6)
C33	9184(17)	5480(16)	3566(18)	62(6)
C34	6759(14)	5500(14)	2772(15)	42(5)
C35	5930(15)	5375(17)	3493(15)	52(5)
C36	5535(16)	6231(16)	3830(16)	56(6)
C37	5978(15)	7261(16)	3457(15)	49(5)
C38	6794(15)	7414(17)	2723(15)	51(5)
C39	7175(15)	6562(15)	2418(15)	51(5)
B	7184(18)	4507(18)	2350(18)	45(6)

<sup>a</sup>Coordinates multiplied by  $10^4$ , temperature factors by  $10^3$ .

The complexes with X = I, NCS, NCO are 1:1 electrolytes in acetone solution (Table II); their absorption spectra in such solvent are similar to the reflectance spectra (Fig. 1A). Although in the case of MeTPyEA cobalt(II) complexes with effective  $C_{3v}$  symmetry it may be difficult to distinguish between pseudotetrahedral and distorted trigonal bipyramidal geometries on the basis of electronic spectra alone [2]; the above TPyEA complexes are most likely five-coordinate based on stoichiometry, conductivity and details of spectral

TABLE V. Selected Bond Distances (Å) and Angles (°) for  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$ .<sup>a</sup>

Co-Br	2.644(3)	Co-N2	2.10(2)
Co-Br'	2.720(3)	Co-N3	2.10(1)
Co-N1	2.27(1)	Co-N4	2.06(2)
Br-Co-Br'	83.3(1)	Br'-Co-N3	87.6(4)
Co-Br-Co'	96.7(2)	Br'-Co-N4	89.5(4)
Br-Co-N1	96.9(4)	N1-Co-N2	89.4(6)
Br-Co-N2	87.8(4)	N1-Co-N3	92.3(5)
Br-Co-N3	170.6(3)	N1-Co-N4	85.6(6)
Br-Co-N4	91.2(4)	N2-Co-N3	90.7(6)
Br'-Co-N1	175.1(3)	N2-Co-N4	174.7(5)
Br'-Co-N2	95.5(4)	N3-Co-N4	91.1(6)

<sup>a</sup>Primed atoms are related to the corresponding unprimed atoms by an inversion center at the origin.

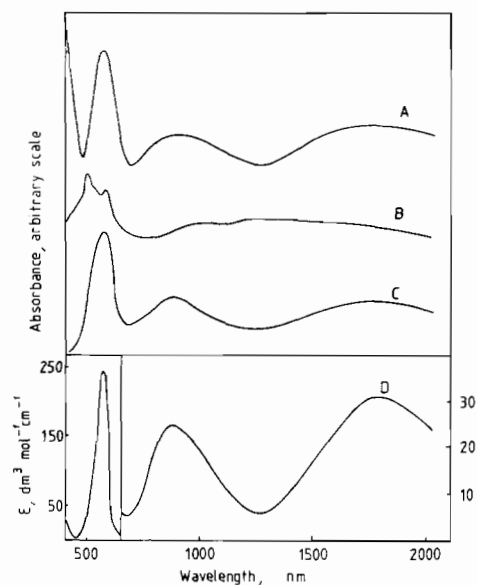


Fig. 1. Diffuse reflectance spectra of:  $[\text{CoI}(\text{TPyEA})]\text{BPh}_4$ , curve A; magenta  $[\text{CoBr}(\text{TPyEA})]_2(\text{BPh}_4)_2$ , curve B; violet  $[\text{CoBr}(\text{TPyEA})]\text{BPh}_4$ , curve C. Absorption spectrum of  $[\text{CoBr}(\text{TPyEA})]\text{BPh}_4$  in acetone, curve D.

features\*. In particular, the absorption at ca. 1800 nm in the spectra of the present cobalt(II) complexes is typical of trigonal bipyramidal geometry; it is shift-

\*The structure of the compound  $[\text{CoI}(\text{TPyEA})]\text{BPh}_4$  in the solid state has been determined by X-ray diffraction. The compound is monoclinic, space group  $P2_1/n$ , with  $a = 17.350(8)$ ,  $b = 16.316(7)$ ,  $c = 13.310(6)$  Å,  $\beta = 95.81(6)$ . Structure solved by heavy-atom methods and refined by full-matrix least-squares with Co, 1 anisotropic and N, C, B, isotropic, to  $R = 6.2\%$  for 2684 observations with  $I > 3\sigma(I)$  (four-circle diffractometer data). The metal atom is in a trigonal bipyramidal environment with the amine nitrogen of TPyEA and the iodine atom in the axial positions (Co-I = 2.76, Co-N<sub>ax</sub> = 2.51, Co-N<sub>eq</sub> = 2.02–2.04 Å). Details are available from the authors.

ed to higher energies in pseudotetrahedral complexes [10, 1d, 2]. Moreover, the molar absorption coefficients of the present compounds, although relatively high, are in most cases well below those found for pseudotetrahedral complexes of cobalt(II). Based also on electronic spectra, the complex  $[\text{Co}(\text{ClO}_4)(\text{TPyEA})]\text{BPh}_4$  is assigned a five-coordinate geometry with the  $\text{ClO}_4^-$  acting as a monodentate ligand. This complex is 2:1 electrolyte in acetone and the electronic spectrum in the same solvent, still indicating five-coordination, is not identical to the spectrum of the solid compound. Presumably, in acetone solution one solvent molecule is bound to the metal replacing the perchlorate ion\*\*.

The complexes with Cl, Br, and  $\text{N}_3$  as coligands have reflectance spectra different to some extent from their absorption spectra in acetone solution (Table II and Fig. 1). The latter, in turn, are quite similar to those of the four complexes discussed above. The complexes are 1:1 electrolytes in acetone, based on the  $[\text{CoX}(\text{TPyEA})]\text{BPh}_4$  formula. If the original pink or magenta complexes are heated in the solid state at appropriate temperatures or are subjected to pressure by grinding (see Experimental), they transform into violet compounds. The electronic spectra of the violet solid compounds are closely similar to those of the parent complexes in acetone solution (Fig. 1C, D). Also the  $[\text{CoF}(\text{TPyEA})]\text{Y}$  pink complexes ( $\text{Y} = \text{BPh}_4, \text{BF}_4$ ) transform to violet compounds by heating. The reflectance spectra of the pink or magenta complexes ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{N}_3$ ) may be suggestive of six-coordination even though they are not typical of octahedral cobalt(II) complexes. Since six-coordination can only be achieved through sharing of donor atoms between metal centers, it could affect the temperature dependence of the magnetic moments of the compounds. Actually, the magnetic moments of the fluoro and azido derivatives decrease with temperature (Table II), but those of the chloro and bromo derivatives do not.

In order to achieve better insight into the structures of compounds of this series, and possibly on the nature of the transformations occurring in the solid state, the X-ray structural determination of the magenta form of the complex of stoichiometry  $[\text{CoBr}(\text{TPyEA})]\text{BPh}_4$  was undertaken.

The structure of the compound consists of dinuclear  $[\text{CoBr}(\text{TPyEA})]_2^{2+}$  cations and  $\text{BPh}_4^-$  anions. The metal atoms in the centrosymmetric cation are bridged by the two bromine atoms. Each metal is further coordinated by the four nitrogen donors of one TPyEA ligand in an overall distorted octahedral

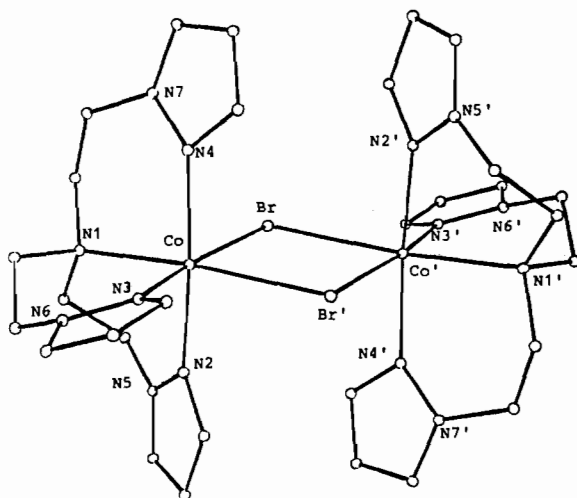


Fig. 2. Schematic representation of the structure of the  $[\text{CoBr}(\text{TPyEA})]_2^{2+}$  cation. Primed atoms are related to the corresponding unprimed ones by an inversion center.

environment (Fig. 2). The length of the  $\text{Co}\cdots\text{Co}$  distance, 4.008(3) Å, allows us to exclude any direct metal-metal interaction. The metal-nitrogen distances are considerably longer (by 0.14 Å in the mean) than those existing in the four-coordinate  $[\text{Co}(\text{MeTPyEA})]_2^{2+}$  cation [2a], but are only slightly longer (ca. 0.02 Å) than those found in the trigonal bipyramidal conformer of the five-coordinate  $[\text{NiBr}(\text{MeTPyEA})]^+$  cation [11]. This may be attributed to the decreased steric hindrances on going from the methylated MeTPyEA to the unmethylated TPyEA ligand. However, the most significant effects of such reduction in the non-bonded interactions involve the coordination number, as no six-coordinate cobalt(II) complex with the methylated ligand has been isolated; all of the complexes so far obtained are four-coordinate except for the five-coordinate  $[\text{Co}(\text{NCS})(\text{MeTPyEA})]\text{BPh}_4$  [11]. The existence in the structure of the present compound of some short  $\text{Br}\cdots\text{C}$  interactions, in the range 3.4–3.5 Å, is indicative of crowding which may disfavour the dimeric vs. monomeric species. Conceivably, the transformation in the solid state exhibited by the bromide as well as by the other complexes listed above, involves an equilibrium between mononuclear and dinuclear species, occurring through cleavage of the metal-bridging ligand bond accompanied by a conformational rearrangement of the facultative tetradentate ligand.

The  $[\text{Co}(\text{NCS})_2(\text{TPyEA})]$  complex is pink and six-coordinate, as indicated by its reflectance spectrum (Table II and Fig. 3A). The complex changes to a blue isomer by grinding and gives a blue solution in acetone. The absorption spectrum in acetone solution (Fig. 3C) is identical to that of  $[\text{Co}(\text{NCS})_4]^{2-}$ ; no

\*\*A cobalt(II) complex of TPyEA with coordinating acetone molecules has been isolated. The X-ray structural determination of this complex is in progress.

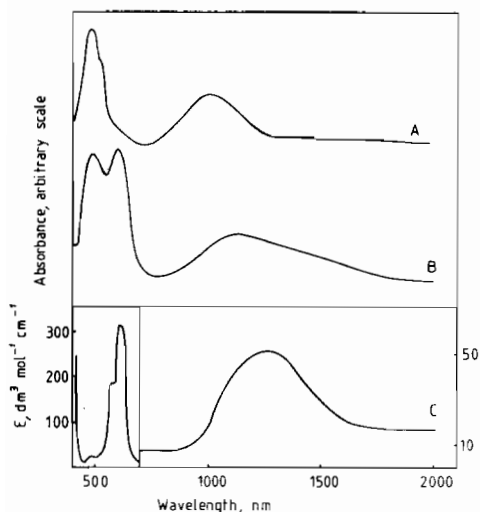


Fig. 3. Electronic spectra of  $[\text{Co}(\text{NCS})_2(\text{TPyEA})]$ : diffuse reflectance spectra of the pink complex, curve A, and of the blue complex, curve B; absorption spectrum in acetone, curve C.

other species can be identified in the absorption spectrum owing to the high absorbance of the tetrahedral cobalt(II). Also the reflectance spectrum of the blue isomer (Fig. 3B) is dominated by the absorption due to a cobalt(II) tetrahedral species; however the band at 490 nm and the high-energy tail of the broad and asymmetric absorption centered at 1125 nm seem to indicate that also a six-coordinate cobalt(II) species is present in addition to the tetrahedral one. On the basis of the electronic spectra alone, however, no conclusion can be drawn concerning the structural change of the bis thiocyanate derivative upon dissolution in acetone or after grinding in the solid state.

Finally, the complexes with bidentate coligands, namely  $[\text{CoY}(\text{TPyEA})]\text{BPh}_4$  ( $\text{Y} = 2\text{-mercaptobenzoate}$ ) and  $[\text{CoY}(\text{TPyEA})]\text{ClO}_4$  ( $\text{Y} = \text{acetylacetonate, benzoylacetonate}$ ) may be safely assigned six-coordinate structures both in the solid state and in solution

based on the nature of the bidentate coligands and on their spectral and magnetic properties (Table II).

### Acknowledgements

Thanks are expressed to Mr. F. Zanobini and Mr. D. Masi for technical assistance, and to Mr. G. Vignozzi for microanalyses. Thanks are due to the I.S.S.E.C.C. Institute, Florence, for use of instruments.

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