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Complexes with Sulphur and Selenium Donor Ligands. Part V. Some Co(II) Complexes with Bidentate and Monodentate Unsubstituted Thiosemicarbazones

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Some thiosemicarbazone complexes of Co(II) halides, of general formula CoL_2X_2 *(*$L = NH_2C(S)NHN{=}CR_1R_2$; $R_1 = R_2 = Me$; $R_1 = Me$, $R_2 = Ph$; R_1R_2 *= cyclohexanone;* $R_1 = H$, $R_2 = Ph$*) have been prepared and characterised. From spectroscopic data it is concluded that when* R_1 *and/or* R_2 *is an aryl group, the structure in the solid state is tetrahedral of chromophore* $[CoS_2X_2]$ *the ligands being monodentate. When* $R_1 = R_2 = Me$ *or cyclohexanone, the solid state structure is trigonal bipyramidal. Independent crystal structure analyses for two examples,* $Co(NH_2C(S)NHN{=}CMe_2)_2Cl_2 \cdot H_2O$ *and* $Co(NH_2C(S)NHN{=}CMePh)_2I_2$ *have confirmed these assignments.*

Possible structures present in solution are discussed.

Introduction

Although thiosemicarbazones, $NH_2C(S)NHN{=}CR_1R_2$, have long been known to give stable complexes with transition metal ions [2], only recently have the stereochemistry and reactions of these complexes been investigated [3]. A reason for this renewed interest is the proved anti-tumour activity of variously substituted formylpyridine thiosemicarbazones, which is believed to be related to their complexation with RDR (Ribonucleoside Diphosphate Reductase) [4].

Of the few structural studies carried out on tsz's**, that on $Ni(atsz)_2Cl_2 \cdot H_2O$ [5] showed the Ni(II) to be trigonal bipyramidal, only one of the chlorine atoms being bonded to the metal, whilst the nitrate analogue is octahedral (assuming that the bonded NO_3^- can indeed be treated as bidentate) [5]. Five-coordinate stereochemistry with Ni(II) has been suggested for various complexes having $R_1 = Me$, $R_2 = Bu$, and R_1R_2 = cycloheptane, on the basis of spectroscopic data [6].

Although there have been scattered reports of Co(II) tsz complexes [6, 7], there has been no attempt to correlate stereochemistry with organic substituent group. We report the characterisation of some Co(II) halide complexes of potentially bidentate tsz's which reveals that these ligands may also behave as monodentate ligands.

Experimental

Thiosemicarbazide (Merck) and the ketones (C. Erba) were reagent grade products and were used as received. The ligands were prepared following the methods described by Sah and Daniels [8]; a typical preparation is described.

A solution of thiosemicarbazide (0.01 mol) in water (30 ml) containing 2 ml acetic acid was heated on a steam bath for a few minutes. This solution was added to a warm solution of the aldehyde or ketone (0.01 mol) in EtOH (25 ml), the mixture heated until clear and then cooled. The crystalline azone was filtered off, washed with 1:1 EtOH–water, dried and recrystallised from an EtOH–water mixture. The *anti*-form of aptsz was used (m.p. 118 °C; lit. [8] 118–9 °C); other m.p.'s agreed with literature values [8].

The complexes were obtained by simply reacting the metal halide with the tsz in ethanol, or, in some cases, acetone; analyses and some properties are listed in Table I. As many of the complexes crystallise with water molecules, they were all analysed by t.g.a.

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**Abbreviations: tsz = a thiosemicarbazone; atsz = acetonethiosemicarbazone; btsz = benzaldehydethiosemicarbazone; aptsz = acetophenone-tsz(*anti*[8]-); ctsz = cyclohexanone-tsz. Numbering: $\underset{4}{N}H_2C(S)\underset{2}{N}H\underset{1}{N}{=}CR_1R_2$.

TABLE I. Analytical Data.

Complex	Colour	Found (%)					Calcd. (%)				
		C	H	N	M	H_2O	C	H	N	M	H_2O
$Co(atsz)_2Cl_2 \cdot H_2O$	Blue	23.59	4.96	20.58	–	4.2	23.42	4.88	20.50	–	4.4
$Co(atsz)_2Br_2 \cdot 2H_2O$	Blue	18.67	4.10	16.81	–	ca. 7.0	18.58	4.26	16.25	–	6.96
$Co(atsz)_2I_2 \cdot 2H_2O$	Pale Violet	15.90	3.52	14.07	10.07	6.0	15.72	3.60	13.75	9.81	5.80
$Co(atsz)_2I_2$	Green	17.02	3.16	14.25	–	–	16.70	3.18	14.60	–	–
$Co(btsz)_2Cl_2$	Turquoise	39.41	3.78	16.97	12.06	–	39.36	3.68	17.21	12.07	–
$Co(btsz)_2Br_2$	Green	33.35	3.15	14.37	9.9	–	33.30	3.11	14.55	10.21	–
$Co(btsz)_2I_2$	Green–Yellow	30.07	2.90	12.91	–	–	28.62	2.68	12.52	8.78	–
$Co(aptsz)_2Cl_2$	Green	41.74	4.51	16.29	–	–	41.87	4.26	16.28	–	–
$Co(aptsz)_2Br_2$	Green	36.04	3.67	14.13	–	–	35.72	3.64	13.89	9.74	–
$Co(aptsz)_2I_2$	Dark Green	30.54	3.29	11.69	8.1	–	30.91	3.14	12.01	8.43	–
$Co(ctsz)_2Cl_2 \cdot 3H_2O$	Light Blue	35.60	5.77	17.0	12.80	9.3	35.61	5.51	17.80	12.49	–
$Co(ctsz)_2Br_2$	Light Blue	30.18	4.67	15.19	10.30	–	29.96	4.64	14.98	10.51	–
$Co(ctsz)_2I_2$	Green	25.73	4.14	12.17	8.50	5.0	24.32	4.34	12.16	8.45	5.20

Those containing water became anhydrous at 90–100 °C, except for $Coaptsz_2I_2 \cdot 2H_2O$ (purple) which lost one H_2O at *ca.* 60 °C and the second one at *ca.* 120 °C, at which temperature the compound turned green in colour. The green compound was also obtained crystalline by diffusion of pet. ether (40 - 60 °C) into an acetone solution of the components.

Physical Measurements

Reflectance spectra were recorded on a Beckmann DK 2A instrument against MgO as reference and solution spectra on a Shimadzu MPS 50L spectrophotometer in matched 1 cm quartz cells. I.r. spectra were recorded on Beckmann IR 11 and Perkin–Elmer 521 instruments as nujol mulls.

Conductivities were measured on a SIS-Halosis FA2-type Kholraush bridge and molecular weights on a Mechrolab osmometer. Magnetic measurements were made by the Gouy method using $CoHg(SCN)_4$ as calibrant [9]. Thermogravimetric analyses were performed on a Du Pont 950 thermal analyser. Cobalt was estimated by EDTA titration [10], and C, H, and N analyses were by the Istituto Superiore di Sanità, Rome.

Results and Discussion

The ligands all gave only 2:1 complexes with Co(II) halides, whatever the mole ratio of reactants used. They decompose in water but are soluble in ethanol and acetone without apparent oxidation to Co(III) during measurements.

Solid State Structures

The reflectance spectra of the compounds fall into two relatively distinct groups (see Table II). Those of btsz and aptsz, *i.e.* the aryl-substituted derivatives, give two systems of bands lying in the ranges 4.5–9.0 kK and 13.0–17.0 kK (1 kK = 1,000 cm^{-1}) with a distribution of relative intensities and absence of any bands in the intermediate region; this indicates the presence of tetrahedral Co(II) [11]. For example, $Co(aptsz)_2I_2$ gives three relatively weaker bands at 4.8, 5.6 and 7.5 kK and (at least) two bands at 13.3 and 15.0 kK, which are very similar to the reflectance spectra of thiourea complexes of Co(II) [12]. The similarity in spectra is even closer for the chloride and bromide analogues of both aptsz and btsz. The average ν_2 and ν_3 positions for these complexes are at too low an energy for bonding by the two nitrogen atoms of the ligands to be likely. (*e.g.* $\nu_2 = 8.8$ kK and $\nu_3 = 16.5$ kK in *trans*-2-(2′-quinoyl)methylene-3-quinuclidinecobalt(II) dichloride, having a $[CoN_2Cl_2]$ chromophore [13]).

Nevertheless, mixed bidentate–monodentate coordination, to give $[CoS_2NX]$ chromophores (no examples of which have been reported to date) cannot be ruled out *a priori.* Consequently, the crystal structure of $Co(aptsz)_2I_2$ has been solved to confirm the conclusions from spectroscopy. The compound indeed has a tetrahedral structure with the aptsz ligands monodentate. The conformation of the ligand is such that the N(4) atom is held away from the metal ion (see Fig. 1) [14].

The ligand is virtually planar and the phenyl group is *cis* to N(4), there being a strong hydrogen bond between N(1) and N(4) (N(1)–N(4) = 2.61 Å). The $[CoS_2I_2]$ unit is a "squashed" tetrahedron with $\widehat{ICoI} = 115.5°$ and $\widehat{SCoS} = 115°$; there seem to be no obvious steric reasons for this distortion.

The very similar reflectance spectra for the other aptsz complexes and those of the $Co(btsz)_2X_2$ series allows them to be also assigned tetrahedral structures with $[CoS_2X_2]$ chromophores. The shift to higher

TABLE II. Electronic Spectra (in kK)[a].

Complex								
$Co(atsz)_2Cl_2 \cdot H_2O$	r	4.5	4.9	5.7	12.8	17.2	19.0	
	a	5.7	7.7	14.1	15.5	17.6sh	18.1	
		(48)	(51)	(392)	(219)	(130)	(194)	
$Co(atsz)_2Br_2 \cdot 2H_2O$	r	4.5	4.9	5.7	13.0	17.2	18.8sh	
	a	5.6	7.4	14.1	15.0	16.7sh	17.1; 17.4	
		(38)	(48)	(573)	(281)	(135)	(208; 198)	
$Co(atsz)_2I_2 \cdot 2H_2O$	r	4.7	4.9	5.9	14.5	18.5	19.6sh	30.3
	a	5.6	7.0	13.7	14.4	16.0; 16.3		
		(24)	(50)	(685)	(401)	(219; 198)		
$Co(atsz)_2I_2$	r	4.4	4.9	5.6	14.1	16.9	18.8	20.3(w)
	a	as for the hydrate.						
$Co(ctsz)_2Cl_2 \cdot 3H_2O$	r	4.4	4.8	5.8	12.3	17.0	18.2sh	
	a	5.5	7.7	14.1	15.5	17.6sh	17.9; 18.1	
		(93)	(59)	(435)	(220)	(166)	(220)	
$Co(ctsz)_2Br_2 \cdot 2H_2O$	r	4.4	4.9	5.5	13.3	17.4	19.0sh	
	a	5.4	7.3	14.2	15.1	16.7sh	17.1; 17.5	
		(49)	(59)	(548)	(261)	(143)	(221; 205)	
$Co(ctsz)_2I_2 \cdot 2H_2O$	r	4.6	4.9	5.5	18.9	17.0sh	18.8	20.4w
	a	5.6	7.0	13.6, 14.2sh		15.9	16.2	20.0w
		(32)	(45)	(562)		(207)	(192)	(40)
$Co(btsz)_2Cl_2$	r	4.7	5.8	7.4	14.4	14.9	16.3	
	a	5.4	6.1sh	7.4	14.0	14.7	15.8	
		(106)	(79)	(58)	(344)	(399)	(406)	
$Co(btsz)_2Br_2$	r	5.5	6.3	7.5	14.0	14.7	16.0	
	a	5.2	6.0sh	7.1	13.6	14.2	15.2	
		(111)	(86)	(76)	(491)	(5.58)	(518)	
$Co(btsz)_2I_2$	r	5.6	6.0	7.5	12.9	14.2	15.2	
	a	5.2	6.0sh	7.0	12.9	13.6	14.6	
		(87)	(80)	(80)	(371)	(560)	(503)	
$Co(aptsz)_2Cl_2$	r	5.7	6.2	7.7	13.8	14.2	15.8	
	a	5.2	6.0sh	7.6	13.9	14.8	16.1	18.2w
		(113)	(93)	(63)	(403)	(416)	(434)	(45)
$Co(aptsz)_2Br_2$	r	5.6	6.0	8.3	13.3	14.0	15.5	
	a	5.2	5.9sh	7.4	13.6	14.2	15.3	17.4sh
		(109)	(83)	(71)	(502)	(581)	(478)	
$Co(aptsz)_2I_2$	r	4.7	5.7	7.5	12.8	13.0	15.0	
	a	5.2	5.8sh	7.0	12.9	13.7	14.5sh	16.7w
		(109)	(93)	(97)	(514)	(812)	(582)	

[a] r = reflectance; a = acetone, ε, in mol l^{-1} cm^{-1} in parentheses (assuming the same species as in the solid, see text); sh = shoulder, w = weak.

energies of the band components of ν_3 in the order Cl > Br > I and the $10Dq_{average}$ parameters (found by König's method [15]), all very similar to those of substituted Co(II) thiourea complexes [16], are in agreement with this assignment. It seems accepted that the structure in ν_2 and ν_3 in CoL_2X_2 complexes results from a reduced symmetry ligand field rather than from spin–orbit coupling [16, 17]. We therefore tentatively assign the bands as, *e.g.* for $Co(aptsz)_2I_2$, 4.7, 5.7 and 7.5 kK to the $^4B_1$, $^4A_2$ and $^4B_2$ components of $^4T_1(F)(T_d)$, and 12.8, 13.0 and 15.0 kK to the $^4B_2$, $^4A_2$ and $^4B_1$ components of $^4T_1(P)(T_d)$, as

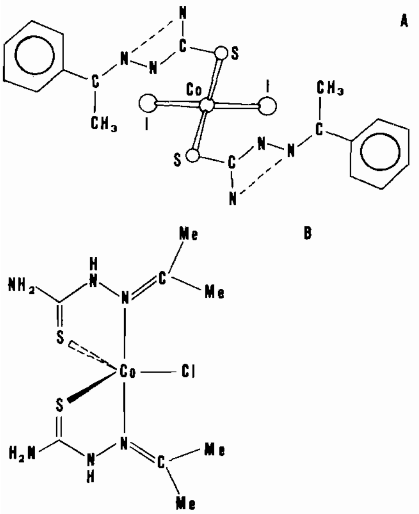

Figure 1. Molecular structures (schematic) of Co(aptsz)$_2$I$_2$ and the Co(atsz)$_2$Cl$^+$ unit of Co(atsz)$_2$Cl$_2$•H$_2$O [14, 22].

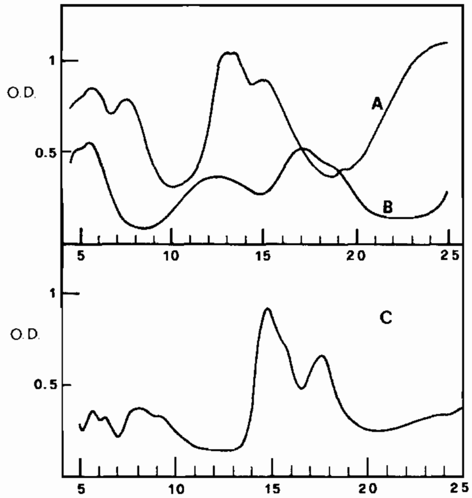

Figure 2. Reflectance spectra. A) Co(aptsz)$_2$I$_2$; B) Co(atsz)$_2$-Cl Cl•H$_2$O; C) Co^{2+}/Zn(atsz)Cl$_2$ (10% Co^{2+}, nominal).

TABLE III. Magnetic Data.

Co(atsz)$_2$Cl$_2$			Co(btsz)$_2$Br$_2$		
T (°K)	μ_{eff} (B.M.)	χ_A 10^6 (cgs)	T (°K)	μ_{eff}	χ_A 10^6
99	4.13	21400	97	4.27	23300
100	4.10	20800	99	4.30	23100
130	4.16	16500	100	4.28	22700
150	4.25	14900	103	4.28	22100
177	4.28	12000	131	4.26	17500
189	4.30	12100	139	4.29	16400
198	4.29	11600	150	4.34	15500
203	4.32	11400	170	4.38	14000
221	4.34	10500	195	4.43	12500
239	4.37	9900	218	4.46	11300
249	4.38	9600	226	4.49	11000
260	4.39	9200	240	4.50	10400
269	4.40	8900	253	4.51	10000
293	4.41	8250	291	4.53	8700
Co(ctsz)$_2$Br$_2$			Co(aptsz)$_2$I$_2$		
95	4.16	22500	102	4.61	25900
96	4.16	22300	109	4.61	24100
115	4.17	19200	123	4.63	21600
133	4.17	16200	141	4.68	19300
141	4.18	15400	151	4.71	18200
167	4.25	13400	158	4.73	17500
177	4.26	12700	173	4.74	16100
184	4.30	12500	189	4.78	15000
197	4.30	11600	196	4.79	14500
201	4.31	11400	206	4.81	13900
210	4.34	11100	216	4.82	13300
224	4.35	10400	225	4.83	12800
233	4.36	10100	233	4.85	12500
248	4.39	9600	243	4.87	12100
267	4.39	8900	259	4.87	11400
289	4.40	8300	289	4.90	10300

for Co(*sym*-diethylthiourea)$_2$Cl$_2$ [16], in approximately C_{2v} symmetry.

During the course of this work, Malik and Phillips reported data for Co(btsz)$_2$X$_2$ (X = Cl, Br) from which they concluded that both of these complexes had bis-chelate structures with ionic halides [18]. The above arguments, confirmed by crystal structure analysis, show that this is not the case.

The reflectance spectra of the atsz and ctsz complexes are very different from those of the aryl analogues (see Fig. 2). Octahedral structures for these complexes may be excluded both from the form of the reflectance spectra and from the low magnetic moments (Table III) [19]. Although the presence of relatively intense bands between *ca.* 11.5 and 13.5 kK is usually taken as diagnostic for five-coordination [20], it is not so easy to distinguish between trigonal bipyramidal and square pyramidal stereochemistries when distortion might be present. Neither stereochemistry with [CoN$_2$S$_2$X] chromophore is known. This difficulty was found previously in an investigation of some tridentate 2-methylthiosemicarbazones of Co(II) [21].

The crystal structure of Co(atsz)$_2$Cl$_2$·H$_2$O has been solved to clarify this point [22]. The complex is trigonal bipyramidal, with the chlorine atom and two sulphur atoms lying approximately in a plane, one of the chlorine atoms being ionic (Fig. 1). (the X-ray powder evidence previously used [18] to deduce a trigonal bipyramidal structure for the Co(II) complex from that for the Ni(II) analogue is misleading; the latter is orthorhombic, the former monoclinic). The close similarity of the spectra of the other atsz and ctsz complexes to that of [Co(atsz)$_2$-Cl]Cl·H$_2$O indicates they have the same structure, *i.e.* a TBP stereochemistry with (approximately) C_{2v} symmetry. The only exception appears to be Co(atsz)$_2$I$_2$·2H$_2$O, which has bands shifted to higher energy than might be expected for a [CoS$_2$N$_2$I] chromophore. This indicates that a water molecule is bonded to the metal ion rather than an iodide. In agreement with this, the water is lost in two steps and the reflectance spectrum of the final product is as expected for a [CoS$_2$N$_2$I] chromophore (tables I and II). By contrast, Co(ctsz)$_2$I$_2$·2H$_2$O loses both H$_2$O at 100 °C and contains bonded iodide.

I.r. band assignments for tsz complexes are difficult to arrive at because of extensive mixing of internal modes of the ligand, *e.g.* deformation modes involving –NH$_2$ are mixed with skeletal bending and stretching modes [2]. Nevertheless, there are differences between the i.r. spectra of complexes having the two stereochemistries which may be of diagnostic value. On complexation, the band at *ca.* 1500–1530 cm^{-1}, believed to arise from (mainly) ν(CN) + δ(NH$_2$) [2], is shifted only slightly in the monodentate complexes (10–20 cm^{-1}; aptsz gives a split band) whilst in atsz and ctsz complexes it shifts to higher frequency by 50–60 cm^{-1}.

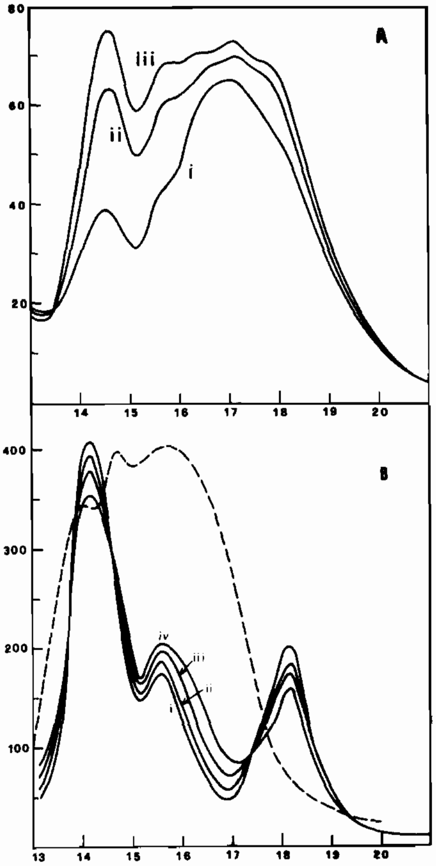

Figure 3. Solution spectra. A) Co(ctsz)$_2$Cl$_2$·3H$_2$O in EtOH, (i) 2 °C; (ii) 25 °C; (iii) 38 °C. B) Co(btsz)$_2$Cl$_2$ in acetone. CoCl$_2$ (anhyd.) + atsz in acetone, (i) 1:1; (ii) 1:1.5; (iii) 1:2; (iv) 1:3.

Solution Structures

Examples of electronic spectra in acetone and ethanol are shown in Fig. 1 and those in acetone are listed in Table II. The aryl derivatives maintain a tetrahedral structure in acetone, the chromophore being again [CoS$_2$X$_2$] since there is little change in spectrum between solid state and solution. In agreement with this, conductance measurements show that all the aryl derivatives are non-electrolytes in acetone. However, the molecular weights are lower than expected which suggest some dissociation with participation of solvent.

The alkyl derivatives give electronic spectra in acetone very different from those in the solid state. For example, Co(atsz)$_2$Cl$_2$·H$_2$O gives weak bands at 5.7, and 7.7 kK in the near-i.r. and a characteristic three-band system (14.1, 15.5 and 18.1 kK) in the visible region, in acetone. There is no detectable change when the spectrum is recorded at 0° – 40 °C, which indicates that only a single species is present. Figure 3 shows that addition of atsz to anhydrous CoCl$_2$ in acetone proceeds through two species, of almost identical chromophore. The spectrum is not one characteristic of five-coordination and since all six alkyl derivatives are non-conducting in acetone, mixed monodentate–bidentate coordination to give $[CoN_2SX]$ or $[CoS_2NX]$ chromophores seems unlikely. The molecular weights in acetone suggest that a chromophore $[CoNSX_2]$ might be present. There are no complexes with this chromophore reported in the literature. However, Co^{2+} dissolves in Zn(atsz)-Cl_2 to form a solid solution and the zinc complex is known to have a tetrahedral monomeric structure with a $[ZnNSX_2]$ chromophore [22]. The reflectance spectrum of this solid solution (Fig. 2) is very similar to the spectrum of $Co(atsz)_2Cl_2 \cdot H_2O$ in acetone. This is further evidence that $Co(atsz)X_2$ species are present in acetone; all attempts to isolate them were unsuccessful.

On solution in ethanol, the alkyl derivatives give two distinct species in equilibrium (Fig. 3). As an example, that of $Co(ctsz)_2Cl_2 \cdot 3H_2O$ in EtOH is consistent with the setting up of the equilibrium:

$$\text{Ligand} + \text{tetrahedral } [CoSNX_2] \rightleftarrows \text{TBP}[CoN_2S_2Cl] + Cl^-$$

In agreement with this, the conductance in EtOH is in the range 20–40 $cm^2\ \Omega^{-}\ mol^{-1}$ (reference, $Et_4NBr = 41$, Ph_4AsCl–EtOH = 58.8 $cm^2\ \Omega^{-1}\ mol^{-1}$).

Conclusions

Steric effects have been invoked to explain the presence of structural changes between five- and six-coordination in complexes of bidentate tsz's [18]. The aryl substituted derivatives are the first examples of tsz's acting as monodentate ligands with transition metal ions. This monodentate behaviour is not confined to Co(II); tetrahedral Ni(II) complexes are also obtainable [24]. Changes in basicity at N(1) are thus an important feature of the coordination behaviour of tsz's.

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References

1 Part IV. L. Gastaldi, P. Porta and A. A. G. Tomlinson, *J. Chem. Soc. Dalton,* 1424 (1974).
2 *E.g.* A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem., 9,* 46 (1964).
3 M. J. M. Campbell, *Coordin. Chem. Revs., 15,* 279 (1975).
4 F. A. French, E. J. Blanz, S. C. Shaddix and R. W. Brockman, *J. Med. Chem., 17,* 172 (1974).
5 M. Mathew, G. J. Palenik, and G. R. Clark, *Inorg. Chem., 12,* 446 (1973).
6 B. Beecroft, M. J. M. Campbell, and R. Greskowiak, *J. Inorg. Nucl. Chem., 36,* 55 (1974).
7 N. V. Gerbeleu, A. V. Ablov, and M. D. Revenko, *Russ. J. Inorg. Chem., 15,* 1235 (1970), and refs. therein.
8 P. T. T. Sah and T. C. Daniels, *Rec. Trav. Chim., 69,* 1545 (1950).
9 P. W. Selwood, "Magnetochemistry", 2nd edn., Interscience, New York (1956).
10 A. I. Vogel, "Quantitative Inorganic Analysis", Longmans, London (1961).
11 R. L. Carlin, *Progress in Inorganic Chem., 1,* 1 (1965).
12 O. Piovesana and C. Furlani, *J. Inorg. Nucl. Chem., 30,* 1249 (1968).
13 G. J. Long and D. L. Coffen, *Inorg. Chem., 13,* 270 (1974).
14 M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Cryst. Struct. Commun., 4,* 629 (1975).
15 E. König, *Structure and Bonding, 9,* 175 (1971); the values found are:

	Dq	B
$Co(btsz)_2Cl_2$	376	700
Br_2	363	670
I_2	362	630
$Co(aptsz)_2Cl_2$	385	680
Br_2	377	650
I_2	364	600

(in cm^{-1})
16 A. A. G. Tomlinson, C. Bellitto, O. Piovesana, and C. Furlani, *J. Chem. Soc. Dalton,* 350 (1972).
17 E. R. Manzel, W. R. Vincent, D. K. Johnson, G. L. Seebach, and J. R. Wasson, *Inorg. Chem., 13,* 2465 (1974).
18 M. A. Malik and D. J. Phillips, *Aust. J. Chem., 28,* 305 (1975).
19 A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1968).
20 I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem., 14,* 812 (1975), and refs. therein.
21 M. A. Malik and D. J. Phillips, *J. Inorg. Nucl. Chem., 36,* 2229 (1974).
22 M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Cryst. Struct. Commun., 5,* 605 (1976).
23 M. Mathew and G. J. Palenik, *Inorg. Chim. Acta, 5,* 349 (1971).
24 G. De Munno and A. A. G. Tomlinson, Unpublished observations.