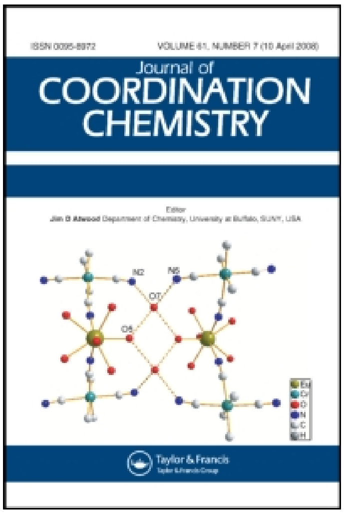

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PSEUDOTETRAHEDRAL COBALT(II)-COMPLEXES OF 2,5-DIMETHYL-1,3,4-THIADIAZOLE

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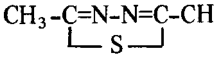
The cobalt(II) complexes of 2,5-dimethyl-1, 3,4-thiadiazole (DTZ) $Co(DTZ)_2X_2$ ($X = Cl, Br, I, NO_3$) have been prepared and investigated. Their observed magnetic moments lie in the range 4.4–4.6 B.M. The complexes have a pseudo-tetrahedral coordination; a threefold splitting of the electronic ν_2 and ν_3 bands of the halide complexes indicate a C_{2v} symmetry. In the nitrate complex the anion is coordinated as monodentate ligand as shown by its infrared bands; however a weak interaction of a second oxygen atom, with a consequent distortion of the pseudo-tetrahedral coordination toward a six-coordination, cannot be excluded. In all these complexes the ligand DTZ is coordinated to the metal ion through one of the two nitrogen atoms. The far i.r. $\nu(CoN)$ and $\nu(CoX)$ (X = Cl, Br, I, O) bands were identified.

INTRODUCTION

Until now no complex of 2,5-dimethyl-1,3,4-thiadiazole



$CH_3\text{-}C{=}N\text{-}N{=}C\text{-}CH_3$

(DTZ) has been investigated, notwithstanding that its pentatomic ring has one sulphur and two nitrogen atoms as potential sites for metal-ion coordination. In order to initiate the study of the coordinating behaviour of this ligand some cobalt(II) DTZ-complexes were prepared and investigated.

EXPERIMENTAL

The complexes $Co(DTZ)_2X_2$ ($X = Cl, Br, I, NO_3$) were prepared by slowly adding a solution of the ligand (0.25 mmole) in ethyl ether (0.5 cm^3) to a warm solution of the cobalt salt (0.1 mmole) in ethanol (1 cm^3) and washing the precipitate with EtOH. The chloride could also be prepared by melting the ligand (2.5 or 4 mmole) and adding anhydrous $CoCl_2$ (1 mmole) to the melt.

The compounds were analysed by standard methods (Table I). Molar conductivities were measured in 10^{-3} M nitromethane solution with a WTW conductivity bridge at 25°C; magnetic susceptivities were determined by the Gouy method and corrected with the Pascal constants (Table I). Infrared spectra (Table II) were recorded on the solids in KBr disks (4000–250 cm^{-1}) and in nujol mulls on polythene (400–60 cm^{-1}) with a Perkin-Elmer 180 spectrophotometer. The electronic spectra (Table III and Figure 1) were recorded on the acetone solutions of

TABLE I
Analytical data, found % (calcd. %); magnetic moments (B.M.) and molar conductivities Λ_M (Ω^{-1} $mole^{-1}$ cm^2) at 25°C in 10^{-3} M nitromethane solution of the cobalt(II) DTZ-complexes

Compound	Color	N	C	H	Λ_M	μ_{eff} (B.M.)	μ^*_{eff}[c] (B.M.)
$Co(DTZ)_2Cl_2$[a]	blue	15.67(15.64)	27.06(26.83)	3.44(3.38)	18	4.41	4.28
$Co(DTZ)_2Br_2$[b]	blue	12.49(12.53)	21.47(21.49)	2.74(2.70)	21	4.51	4.38
$Co(DTZ)_2I_2$	green	10.20(10.35)	17.39(17.76)	2.36(2.24)	27	4.57	4.44
$Co(DTZ)_2(NO_3)_2$	violet	20.32(20.43)	23.04(23.36)	2.89(2.94)	17	4.39	4.27

[a] Co % = 16.45(16.45).

[b] Co % = 13.31(13.18).

[c] μ^*_{eff} is the value of μ_{eff} corrected for T.I.P. = 2.09/10 Dq c.g.s.u. (Table III).

TABLE II
Principal infrared bands (cm^{-1}) of DTZ and its complexes

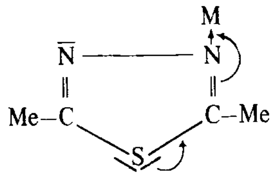
	DTZ	$Co(DTZ)_2Cl_2$	$Co(DTZ)_2Br_2$	$Co(DTZ)_2I_2$	$Co(DTZ)_2(NO_3)_2$
		686mw	682m	682mw	685m
ν(CS)	642vs	656s	652s	652s	656s
	518m	520mw	518m	519m	520m
Ligand bands ($<$650 cm^{-1})	362s	374m	374m	373wm	375m
	278s	282s	287s	284s	284sh
	197mb	193mb	188mwb	180wb	184ms
	82m				86mb
	55m		56wm		
ν(MX)		336vs	262s	232s	306sh
		313s	244s	(220m, sh)	294vsb
ν(MN)		252w	(244s)	(232s)	268sh
		221m	223mw	220m, sh	236mb
def. (N.M.N.)		151wm	150w	150w	152w
			141w		141w
δ (MX)		112ms	79m		
		106ms	73sh		

the compounds in quartz cells and on the solid complexes in nujol mulls on filter paper with a Shimadzu MPS-50L spectrophotometer. The electronic spectrum of the nitrate in the region 1800–250 cm^{-1} was also recorded in nujol mull on a KBr disk in order to avoid the presence of the ionic NO_3^- i.r. bands, observed when the powder of the $Co(DTZ)_2(NO_3)_2$ complex is pressed in KBr disks, due to formation of KNO_3.

RESULTS AND DISCUSSION

The molar conductivities (Table I) of the $Co(DTZ)_2X_2$ (X = Cl, Br, I, NO_3) complexes in acetone solution (Table I) (Λ_M = 17–27) indicate that they behave as non-electrolytes (the Λ_M values for 1:1 electrolytes in acetone being 100–140),[1] and that the anions are coordinated to the metal. The magnetic moments at room temperature (Table I) lie in the range (4.4–4.7 B.M.) characteristic for a tetrahedral coordination[2,3] and increases in the anion order $NO_3^- \leqslant Cl^- < Br^- < I^-$.

The infrared spectra of the four compounds are almost identical indicating that the complexes have the same structure and the same type of coordination of the ligand to the metal. As all the atoms involved in the coordination belong to the same ring the frequency shifts of the ligand bands in the complexes depend on the composite nature of the bands and cannot be simply related to a single type of bond. However the strong ligand band at 642 cm^{-1}, which is well isolated in the spectrum and does not have other neighbouring bands which are shifted in the complexes, corresponds in the complexes to a strong band at 652–656 cm^{-1} and a medium band at 682–686 cm^{-1}. It is reasonable to assign to this ligand band a high contribution of ν(CS) vibration; its splitting and frequency increase in the complexes are attributable to a coordination of the ligand through one of the nitrogen atoms which increases in different measure the double bond character of the C–S bonds by introducing in the molecule a dissymmetry such as:



The infrared spectrum of the nitrate in nujol mull indicates that the NO_3^- group is coordinated as a monodentate ligand:

	ν_4	ν_1	ν_2
NO_3^- bands	1504m, sh	1267s	1011s
	ν_6	ν_3	ν_5
	800ms	745m	718w cm^{-1}
	ν_4	ν_1	ν_2
NO_3^- monodentate[4]	1550–1410	1290	1000
	ν_6	ν_3	ν_5
	800	740	715

TABLE III

Electronic spectra of the pseudo-tetrahedral cobalt(II) DTZ-complexes in acetone solution and in the solid state and their crystal field parameters calculated with the ν_2 and ν_3 average values of the solids spectra

		Calcd. ν_1	$\nu_2{}^a$ (ϵ)	$\nu_3{}^a$ (ϵ)	Dq[a]	B[a]	β[b]	T.I.P.[c]	$-\lambda$[a,d]
Co(DTZ)$_2$Cl$_2$	solut.		5720(26), 7020(25), 8160(20)	14770(1160), 15975(1120), 17270(880)					
	solid		6100ms, 7435ms, 9130ms	15505s, 16210s, 17270s					
	av.	4320	7425	16130	432	706	0.73	484	114
Co(DTZ)$_2$Br$_2$	solut.		5700(85), 6730(89), 7840(83)	14990(272), 15455(245), 16585(147)					
	solid		5970m, 7195ms, 8795ms	15245s, 15675s, 16750ms					
	av.	4270	7325	15800	427	688	0.71	489	141
Co(DTZ)$_2$I$_2$	solut.		5880(22), 6450(24), 7550(22)	14370(276), 14925(240), 15800(148)					
	solid		5860m, sh, 7140ms, 8510ms	14410s, 14990s, 15950ms					
	av.	4230	7260	15105	423	645	0.66	494	156
Co(DTZ)$_2$(NO$_3$)$_2$[e]	solut.		7470(12), 8790(11)	18800(102), 21010(57)					
	solid		7550w, sh, 8970m	18900s, 20490ms, sh					
	av.	5040	8665	19160	504	847	0.87	415	130

[a] cm^{-1}.

[b] B$_0$:Co = 971.[19]

[c] T.I.P. = 2.09/10Dq c.g.s.u.[19]

[d] $-\lambda = (10Dq/15.48)(\mu^*_{eff} - 3.87)$ cm^{-1}.[19]

[e] Other bands: in solution 14080,[9] in the solid 14490vw.

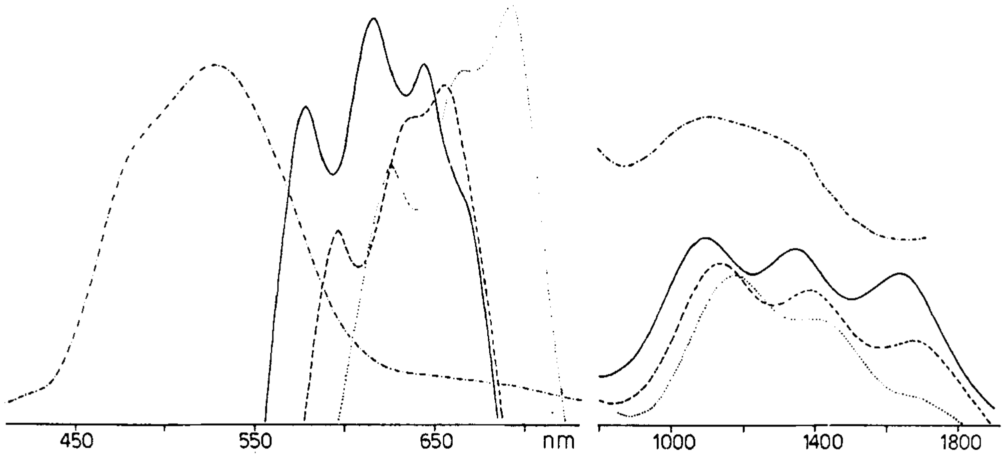


FIGURE 1 Electronic spectra of the solid DTZ-complexes (absorbance in ordinate): (————) $Co(DTZ)_2Cl_2$, (– – – – –) $Co(DTZ)_2Br_2$, (········) $Co(DTZ)_2I_2$, (– · – · – · –) $Co(DTZ)_2(NO_3)_2$.

The far infrared spectra show the ν(CoX) (X = Cl, Br, I) bands in the expected position for terminal Co–X bonds[5–8] with frequency ratios:

ν(CoX) 336:262:232 = 1:0.78:0.69
313:244:220 = 1:0.78:0.70
δ(CoX) 112:79 = 1:0.71
106:73 = 1:0.69

in the range accepted for complexes with similar structures.[9]

The ν(Co–O) frequencies agree well with the values given for other $CoL_2(NO_3)_2$ complexes.[10] The bands assignable to ν(Co–N) modes are in the frequency range given for other similar ligands.[11–14]

In the electronic spectra of the solid halide complexes (Table III and Figure 1) the position of the two polyhumped bands is typical of a distorted tetrahedral coordination and their splitting into three distinct bands indicates a C_{2v} symmetry.[15,16] The spectra of all the complexes in acetone solution are very similar to those of the solids, even if the splitting of the ν_2 and ν_3 bands is less distinct in solution than in the solid state, indicating that the coordination in both cases is the same. The crystal field parameters were calculated with the averaged values of the ν_2 and ν_3 bands of the solids spectra, taking the centre of gravity of the total intensity[17] by using the method of Underhill and Billing.[18] The values of the crystal field parameters agree well with the spectrochemical order for tetrahedral cobalt(II) complexes:[19]

$$NO_3^- > Cl^- > Br^- > I^-$$

that is, in the reverse order of the magnetic moments.

The spectrum of the nitrate complex is rather different from the other three: the splitting of the ν_2 and ν_3 bands does not correspond to a true C_{2v} symmetry for this complex, a weak broad band appears at 14000–14500 cm^{-1} and the Dq and B parameters are rather high with respect to the values[19] of the $[Co(NO_3)_4]^=$ (Dq = 466, B = 755 cm^{-1}) and of the $[Co(N_3)_4]^=$ (Dq = 392, B = 658 cm^{-1}) complexes. Even if the infrared spectra indicate that the NO_3^- group coordinates as a monodentate ligand, weaker interactions of a second oxygen atom may be sufficient to alter the pseudo-tetrahedral geometry of the complex toward a distorted six-coordination; this occurs in a much clearer way in other complexes of tetramethylthiourea and ethylenethiourea, such as $Co(TMTU)_2(NO_3)_2$, $Co(ETU)_2(NO_3)_2$[20] and $Co(ETU)_2(OAc)_2$,[21] for which a coordination intermediate between the octahedral and the tetrahedral has been demonstrated. In these cases, however, the electronic spectra are definitely different from both the tetrahedral and the octahedral ones.

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