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Coordination Compounds of 1-Methylimidazoline-2-(3H)-thione and Metal Nitrates [M(II) = Co, Zn and Cd]. A spectroscopic, Thermal Analysis and X-Ray Diffraction Study

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The synthesis of a number of coordination compounds involving the ligand, 1-methylimidazoline-2(3H)-thione, (MImT = L), with M(II) nitrates (M = Co, Zn and Cd), is described. Compound stoichiometries are $M(MImT)_4(NO_3)_2$ and $Co(MImT)_2(NO_3)_2$. The new compounds are characterised by chemical analysis, infrared spectroscopy and thermal analysis. The Co(II) compounds have also been studied by room temperature magnetic measurements and electronic spectra. Electrolytic conductivities suggest that all the compounds with 1:4 stoichiometry exhibit ligand–nitrate exchange in nitromethane. Thermal analysis indicated the presence of H_2O in $M(MImT)_4(NO_3)_2$ (M = Co(II) and Zn(II)); all of the compounds exhibit similar but complex thermal decompositions. A single-crystal X-ray study has confirmed the presence of an uncoordinated H_2O molecule in $Co(MImT)_4(NO_3)_2H_2O$. The compound also contains ionic nitrate groups and a slightly distorted tetrahedral cation with Co–S contacts to the ligand. H-atoms from the imido(NH) groups and the H_2O molecule together with O-atoms from the nitrate groups are involved in extensive H-bonding.

Introduction

The competitive ligating abilities of heterocyclic molecules and nitrate ions have produced a variety of compounds involving ionic and coordinated nitrate.

With heterocyclic N-donors such as imidazole (Imz) and thiazole (tz) [1–4], both ionic nitrate $[Ni(Imz)_6](NO_3)_2$ and monodentate nitrate $[ML_4(NO_3)_2]$, (L = Imz and tz, M = Cu and Zn) are formed in octahedral species. Both mono and bidentate nitrate are reported [4, 5] for $[NiL_3(NO_3)_2]$, in solution , (L = 4-methylthiazole).

Heterocyclic S-donors such as ethylenethiourea (etu), form square-planar, $[Ni(etu)_4](NO_3)_2$, [6], and tetrahedral, $[Cu(etu)_4](NO_3)_2$, [7], both containing ionic nitrate. Thiazolidine-2-thione, (tzt), on the other hand, forms tetrahedral compounds containing ionic nitrate, $[M(tzt)_4](NO_3)_2$, (M = Co, Zn and Cd) and octahedral $[Ni(tzt)_4(NO_3)_2]$ containing monodentate nitrate [8].

The ability of thiourea (tu) [9], and its tetramethyl derivative (tmtu) [10], to produce compounds containing either coordinated or ionic nitrate is well known. Such behaviour prompted us to study the possibility of similar behaviour for MImT with M(II) nitrates [M(II) = Co, Ni, Zn and Cd]. The Ni(II) compound, $Ni(MImT)_4(NO_3)_2$, is diamagnetic, contains a square planar NiS_4 entity, as well as weakly coordinated nitrate, and is reported elsewhere [11]. Similarly, the crystal and molecular structure of $Zn(MImT)_4(NO_3)_2$, as the monohydrate, is also reported elsewhere [12].

Experimental

Starting Materials

The ligand was used as supplied by Ralph Emmanuel Ltd. Hydrated metal nitrates were of reagent quality.

Preparations

All the 1:4 (metal/ligand) compounds were prepared by dissolving 2 mmol of the hydrated metal nitrate in a small volume (<10 ml) of hot anhydrous ethanol containing 3 ml of triethylorthoformate as dehydrating agent. To this solution the stoichiometric quantity of ligand was added dissolved in the minimum volume (<5 ml) of hot anhydrous ethanol. The total volume was reduced slightly then cooled to room temperature. Subsequent slow evaporation of the solvent produced a crystalline product in each instance, which was removed, washed with a small

TABLE I. Analytical and other Physical Data.

Complex	Colour	Analysis %^{a}			Λ_M^{b} (Ω^{-1} cm^2 mol^{-1})	M.P. (°C)
		C	H	N		
$CoL_4(NO_3)_2H_2O$	Green	29.7(29.5)	4.1(4.0)	22.3(21.3)	9.4	133
$CoL_2(NO_3)_2$	Blue	23.9(23.4)	3.0(2.9)	20.9(20.4)	6.4	180
$ZnL_4(NO_3)_2H_2O$	Colourless	29.8(29.0)	4.1(3.9)	22.4(21.1)	14.0	145
$CdL_4(NO_3)_2$	Colourless	27.7(27.7)	3.5(3.5)	20.2(20.2)	24.0	145

^{a}Calculated values in parentheses. $^b10^{-3}$ M in nitromethane.

TABLE II. Infrared Absorption Bands (cm^{-1}).

Complex		ν(N–H)	Thioamide IV	ν(M–L)	Nitrate bands
$CoL_4(NO_3)_2H_2O$		3100s	745sh 730m	310m	1355s, 1020w, 830m
$CoL_2(NO_3)_2$		3250s	730m	315m	1360s, 1250w, 1020w, 835m, 805w, 750m
$ZnL_4(NO_3)_2H_2O$		3180s	740m	325m	1360s, 1020w, 830m 710w
$CdL_4(NO_3)_2$		3120s	745m	300m	1360s, 1020w, 830m, 730w
Ligand	SOLID	3105s	740m 765sh	–	–
	SOLUTION	3450s	–	–	–

volume of ethanol and finally vacuum dried at room temperature.

$Co(MImT)_2(NO_3)_2$ was prepared in a similar manner but with ethyl acetate as solvent.

Physical Methods

Chemical analysis for C, H and N were performed by Butterworths Microanalytical Services Ltd.

Electrolytic conductivities, infrared and electronic spectra, magnetic measurements and X-ray powder photographs were all performed as has been previously described [13]. Thermogravimetric analyses were performed on a Stanton Redcroft 750 thermobalance in flowing air (5 ml m^{-1}) and a heating rate of 10 °C m^{-1}. Sample sizes were in the range 2–5 mg; Pt crucibles were used for all the compounds.

Results and Discussion

General

Table I lists the compounds with their colours, analytical data, conductivities and melting points. The analytical data show good agreement with the suggested formulae. The presence of a water molecule in the Co and Zn (1:4) compounds was unexpected but was initially indicated by thermal analysis.

The conductivity data shows all the complexes to be non-conductors in nitromethane; which suggests the nitrate groups to be coordinated in solution and possibly in the solid also. It is known however, that in some instances, ionic nitrate will replace monodentate ligands, in solution, by means of reactions of the type:

$$\underset{\text{(solid)}}{[ML_4](NO_3)_2} \rightarrow \underset{\text{(solution)}}{[ML_2(NO_3)_2] + 2L}$$

For $[Ni(etu)_4(NO_3)_2]$ the resulting compound in nitromethane, $[Ni(etu)_2(NO_3)_2]$, is octahedral with bidentate nitrate ions [6]. $Co(MImT)_4(NO_3)_2$ undergoes a striking colour change in nitromethane (green to violet-blue) producing a solution very similar to that of $Co(MImT)_2(NO_3)_2$, in the same solvent. This would seem to support the conductivity data in suggesting that ligand–nitrate exchange is occurring for these 1:4 complexes in solution.

Infrared Spectra

Table II lists the infrared absorptions due to N–H, thioamide IV, metal-ligand stretching and the nitrate bands.

The position of ν(N–H) in these compounds is slightly different from those observed for the MImT halo and perchlorate compounds of Co(II) and

TABLE III. Magnetic Moments, Electronic Spectra, Spectral Band Assignments and Ligand Field Parameters.[a]

Compound	μ (B.M.)	ν_3 (cm^{-1})	ν_2 (cm^{-1})	ν_1 (cm^{-1})[b]	B$'$ (cm^{-1})	β
$CoL_4(NO_3)_2H_2O$	4.53	14492	6666	3845	641	0.66
$CoL_2(NO_3)_2$	4.57	16260	7300	4240	723	0.75
$CoL_2(NO_3)_2$ in nitromethane[c]	–	18519	8547	4980	808	0.84
Assignments		$^4A_2 \rightarrow {}^4T_1(P)$	$^4A_2 \rightarrow {}^4T_1(F)$	$^4A_2 \rightarrow {}^4T_2(F)$		

[a] B is 967 cm^{-1} for the free Co(II) ion [20]. [b] Calculated values [21]. [c] 10^{-3} *M* solution.

Zn(II) [13], the exception being $Co(MImT)_2(NO_3)_2$. The bands are very broad and indicative of intermolecular H-bonding in all probability involving the ligand and nitrate groups.

As has been previously observed for MImT four thioamide bands appear in the range 1465 to 730 cm^{-1} [13]. Analysis of these bands has provided a useful means of characterising metal–ligand contacts for MImT and similar ligands [14, 15]. The most diagnostically useful of these bands for MImT complexes is thioamide IV. In the free ligand it consists of a peak at 740 cm^{-1} and a broader weaker component at 765 cm^{-1}. In nearly all of the compounds the broad component collapses into a peak which now occurs in the range 730 to 745 cm^{-1}, leaving, in one instance, a residual shoulder.

An exception to this behaviour is $Co(MImT)_2(NO_3)_2$ which shows two clearly resolved peaks at 730 and 750 cm^{-1}. However, this region of the spectrum is complicated by the presence of a ν_4 (ionic nitrate) band, which could be split upon coordination [15, 16]. In view of the predominant contribution of ν(C$\cdots$S) to thioamide IV the evidence suggests that coordination occurs through the thione-S atom in these complexes. This is supported by the appearance of ν(M–L) absorptions in the region 300 to 325 cm^{-1}. Such bands have been shown to be characteristic of thione-S coordination for other MImT complexes [12, 13, 18].

All the compounds show three absorptions characteristic of ionic nitrate [16, 17] (Table II) in the range 1355 cm^{-1} (ν_3), 1020 cm^{-1} (ν_1) and 830 cm^{-1} (ν_2). In addition, the Zn and Cd compounds exhibit the ν_4 band in the range 710 to 730 cm^{-1}. The major differences in the nitrate spectra occur for $Co(MImT)_2(NO_3)_2$. This compound exhibits two of the bands associated with coordinated nitrate, namely, ν_1 at 1250 cm^{-1}, ν_6 at 805 cm^{-1} in addition to the splitting of the ν_4 (ionic nitrate) band described previously. Consequently only $Co(MImT)_2(NO_3)_2$) contains coordinated nitrate.

Magnetism and Electronic Spectra of the Co(II) Compounds

Room temperature magnetic moments, diffuse reflectance spectra as well as the solution spectrum of $CoL_2(NO_3)_2$ are reported in Table III together with ligand field parameters and spectral band assignments.

The room temperature magnetic moments are in accord with those of tetrahedral Co(II) complexes of MImT [13] as well as other ligands [19].

The ν_3 band of the hydrated compound showed no splitting while that of $CoL_2(NO_3)_2$ was clearly split. This suggests the former complex has a regular, CoS_4, tetrahedral structure while the latter has a pseudotetrahedral, CoS_2O_2, arrangement, in the solid state.

The observed values of ν_3 and ν_2 were used to calculate D_q and B$'$ by means of the equations of Underhill and Billing [21]. These values confirm that the hydrated compound possesses a CoS_4 tetrahedral chromophore since the values of Dq and B$'$ are very similar to those reported for $[Co(MImT)_4](ClO_4)_2$ (402 and 651 cm^{-1}, respectively) [13]. The derived values for $CoL_2(NO_3)_2$ show ν_1 to be close to that expected from the averaged environment of NO_3^- and MImT ($Co(NO_3)_4^{2-}$, (D_q = 466 cm^{-1}, B$'$ = 755 cm^{-1}). The values for B$'$ and β strongly suggest the presence of coordinated nitrate in this compound.

Both compounds exhibit shifts in their absorption bands in nitromethane. For the ν_3 absorption the shifts range from 690 nm (solid) to 570 nm (solution), for the hydrated compound, and from 615 nm (solid) to 540 nm (solution), for the bis-ligand compound. Both compounds effectively exhibit the same visible spectrum in nitromethane and presumably adopt the same structure. Table III shows the positions of the ν_3 and ν_2 bands of the $CoL_2(NO_3)_2$ compound in nitromethane with the ν_1 and B$'$ values derived as before [21]. The data show that all the bands exhibit a significant shift towards the ultra-violet. This suggests that, in solution, additional interactions may occur between the Co(II) ions and oxygen atoms from each of the nitrates causing a change from pseudo-tetrahedral to pseudo-octahedral geometry. Similar changes have been shown to occur with Co(II) and other S-donor ligands in compounds containing nitrate ion [10] and acetate [22].

For the hydrated Co(II) compound dissolution in nitromethane involves, as shown from the conduc-

TABLE IV. Thermogravimetric Analysis.

Compound	Decomposition Temp. Range (°C)	End Product	Overall Weight Loss (%)		Stepped Weight Losses		
			Th	Obs	T (°C)	%(TG)	%(DTG)
$CoL_4(NO_3)_2H_2O$	35–600	CoS_2	80.5	81.0	51	2.5	2.7
					192	20.5	19.1
					350	27.0	31.5
					548	31.0	27.8
$CoL_2(NO_3)_2$	133–620	CoS_2	70.1	70.5	157	20.0	17.5
					360	27.0	30.0
					575	23.5	23.0
$ZnL_4(NO_3)_2H_2O$	50–812	ZnO	87.7	87.0	66	2.5	3.3
					250	25.0	26.8
					360	29.5	30.4
					637	30.0	26.5
$CdL_4(NO_3)_2$	120–780	CdO	81.5	80.0	157	21.0	21.0
					310	25.0	15.5, 6.1
					705	34.0	36.9

tivity data, exchange between two ligand molecules and two nitrate ions, followed by the additional contacts described above.

Thermal Analysis

Thermal analysis data are listed in Table IV. Figure 1 illustrates TG and DTG data curves for hydrated $Co(MImT)_4(NO_3)_2$.

Overall weight losses show good agreement between the theoretical and the observed values thus confirming the compound stoichiometries. End products were identified by X-ray powder diffraction. Subsequent heating of the decomposition products of the Co(II) complexes produces CoO.

The presence of a water molecule in the hydrates was indicated by initial weight losses on both TG and DTG curves. Subsequent thermal decomposition of these and the anhydrous compounds involved three stages. Agreement between the stepped weight losses from the TG and the DTG curves are generally acceptable for the first of these stages and the observed differences for the remaining decompositions are attributed to peak overlap on the TG curves.

Consideration of the relative molar masses involved for $CoL_2(NO_3)_2$ suggests 2/3 of a ligand molecule to be lost in the first stage. Loss of nitrate occurs in the second stage and the remaining ligand fractions 4/3, are lost in the final, oxide, stage. For $CoL_4(NO_3)_2$ the three stages also involve fractional ligand loss (1-1/3), nitrate and futher ligand loss (2/3) and the final stage, to the oxide, involves removal of the remaining ligands (2).

Such complex decomposition processes are common for coordination compounds containing organic ligands [23, 24] particularly in the presence of nitrate [25].

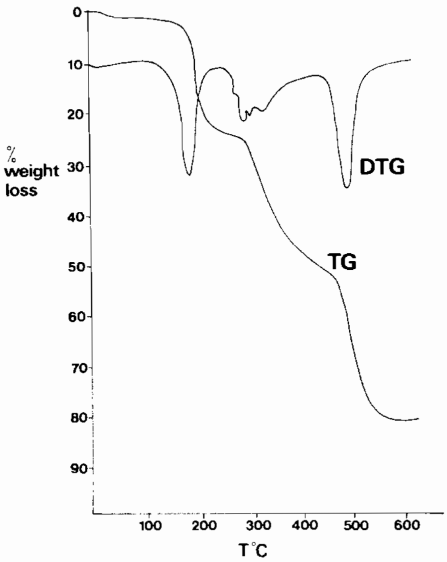

Fig. 1. TG and DTG curves of $Co(MImT)_4(NO_3)_2H_2O$.

The presence of CoS_2 in the residues from the Co(II) compounds suggests that the decomposition involves thermal breakdown of the ligand.

Decomposition processes for the remaining tetra-ligand compounds are similar to the one described.

Crystal and Molecular Structure of $Co(MImT)_4(NO_3)_2H_2O$

Crystal data

Grass-green, well formed crystals of the compound were obtained from the preparation described in the

TABLE V. Bond Distances (A) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code

None x, y, z; (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iii) $-x, -y, -z$.

The Coordination Sphere

(a) Bond distances (A)		(b) Bond angles (°)			
Co–S(1)	2.314(3)	S(1)–Co–S(2)	126.0(1)	Co–S(1)–C(21)	104.4(4)
Co–S(2)	2.321(3)	S(1)–Co–S(3)	101.9(1)	Co–S(2)–C(22)	101.6(4)
Co–S(3)	2.340(3)	S(1)–Co–S(4)	101.3(1)	Co–S(3)–C(23)	103.0(4)
Co–S(4)	2.329(4)	S(2)–Co–S(3)	102.0(1)	Co–S(4)–C(24)	105.4(4)
		S(2)–Co–S(4)	103.3(1)		
		S(3)–Co–S(4)	124.9(1)		

Geometry of the four ligand molecules (X = 1 to 4)

(a) Bond distances (A)

	X = 1	X = 2	X = 3	X = 4
S(X)–C(2X)	1.741(13)	1.754(15)	1.717(11)	1.710(11)
C(2X)–N(1X)	1.340(16)	1.344(19)	1.344(13)	1.358(13)
N(1X)–C(1X)	1.447(15)	1.482(17)	1.420(18)	1.411(16)
N(1X)–C(5X)	1.395(20)	1.409(19)	1.369(17)	1.387(15)
C(5X)–C(4X)	1.388(23)	1.350(21)	1.400(20)	1.365(16)
C(4X)–N(3X)	1.379(23)	1.383(23)	1.390(17)	1.376(14)
N(3X)–C(2X)	1.358(14)	1.346(15)	1.358(16)	1.360(16)

C(4)–H(4)	1.01*	C(4)–H(5)	1.18*	N(3)–H(3)	0.94*

(b) Bond angles (°)

S(X)–C(2X)–N(1X)	129.7(8)	128.7(9)	127.7(9)	126.7(9)
S(X)–C(2X)–N(3X)	123.7(9)	125.7(11)	124.6(8)	126.6(8)
C(X)–N(1X)–C(2X)	125.6(11)	125.6(12)	123.5(10)	126.2(9)
C(1X)–N(1X)–C(5X)	122.6(12)	123.2(13)	127.6(10)	125.6(8)
N(3X)–C(2X)–N(1X)	106.5(10)	105.6(12)	107.7(9)	106.7(9)
C(2X)–N(1X)–C(1X)	111.8(10)	111.1(10)	108.8(10)	108.2(9)
N(1X)–C(5X)–C(4X)	104.0(14)	104.8(14)	108.8(10)	108.8(9)
C(5X)–C(4X)–N(3X)	108.4(14)	108.3(13)	104.1(12)	105.5(11)
C(4X)–N(3X)–C(2X)	109.2(11)	110.1(12)	110.4(10)	110.7(9)

H(4)–C(4)–C(5)	139.6*	H(3)–N(3)–C(2)	115.8*
H(5)–C(5)–C(4)	121.4*	H(3)–N(3)–C(4)	134.6*
H(4)–C(4)–N(3)	123.0*		
H(5)–C(5)–N(1)	135.3*		

Nitrate groups

(a) Bond distances (A)		(b) Bond Angles (°)	
N(1)–O(11)	1.25(2)	O(11)–N(1)–O(21)	119.0(15)
N(1)–O(21)	1.67(2)	O(21)–N(1)–O(31)	118.4(18)
N(1)–O(31)	1.18(2)	O(31)–N(1)–O(11)	122.6(15)
N(2)–O(12)	1.24(2)	O(12)–N(2)–O(22)	118.4(18)
N(2)–O(22)	1.24(2)	O(22)–N(2)–O(32)	122.5(15)
N(2)–O(32)	1.23(2)	O(32)–N(2)–O(12)	119.1(15)

Non-bonding distances (A)

S(21)····S(22)	4.129	O(11)····O(21)	2.09
S(22)····S(23)	3.623	O(21)····O(31)	2.02
S(23)····S(24)	4.140	O(31)····O(11)	2.13
S(24)····S(21)	3.589	O(12)····O(22)	2.13
S(21)····S(23)	3.615	O(22)····O(32)	2.17

(continued overleaf)

TABLE V. *(continued)*

S(22)····S(24)	3.648	O(32)····O(12)	2.13
S(21)····S(21^{iii})	3.808		
Hydrogen bonding (A)			
H(31)·····O(12^{ii})	2.19	H(33)·····O(11^{i})	2.21
H(31)·····O(22^{ii})	2.74	H(33)·····O(31^{i})	2.19
H(32)·····O(12)	2.84	H(34)·····O(11^{i})	2.01
H(32)·····O(32)	2.19	H(34)·····O(21^{i})	2.55
O(99)·····O(11)	3.29		
O(99)·····O(31^{iii})	3.03		
O(99)·····O(31)	2.93		

*Averaged values.

experimental section. Cell constants were obtained from Weissenberg and precession photographs; systematic absences uniquely defined the space-group as *Pbca*. $CoC_{16}H_{26}N_{10}S_4O_7$ (Rel. Molar Mass 657.3), a = 20.683(7), b = 12.657(5), c = 22.112(8) Å, U = 5788.2 Å^3, Dc = 1.52 g cm^{-3}, Dm = 1.53 g cm^{-3}, μ (MoK$_\alpha$) = 8.68 cm^{-1}, $F_{(000)}$ = 2680, Z = 8.

Data collection and reduction

A crystal of dimensions 0.5 × 0.5 × 0.3 mm was mounted with the b-axis coincident with the rotation (ω) axis of a Stoe Stadi-2 two-circle diffractometer. Using monochromated Mo-K$_\alpha$ radiation and the background-ω scan-background technique, 4236 unique reflections were measured, of which 2261 had $I > 2\sigma(I)$ and were considered to be observed. Data were corrected for Lorentz and polarisation but not for absorption effects.

Structure determination and refinement

The Co atom position was determined from a three-dimensional Patterson function and the remaining atoms were located from successive electron-density maps. Methyl H-atoms were included in positions calculated from the molecular geometry (C–H = 1.08 Å); positional parameters of the H-atoms attached to the ligands were included in the calculations. Common isotropic temperature factors were applied to the ethylenic-, methyl- and imido-H atoms which were refined to final values of U = 0.120(20), 0.153(37) and 0.056(12) Å^2 respectively. Scattering factors for all atoms were calculated using an analytical approximation (International Tables for X-ray crystallography, 1974) [26]. The weighting scheme used was, $w = 1.4034/[\sigma^2(F_o) + 0.0022(F_o)^2]$. Full-matrix refinement gave R = 0.0646 and R_w = 0.0666. The final difference map showed no peaks > 0.24 eÅ^{-3}.

All calculations were performed on the NUMAC IBM 370/167 computer at the University of Newcastle upon Tyne. SHELX and related programs were used in the analysis.

[Final atomic parameters, anisotropic temperature factors, observed and calculated structure factors and equations of mean planes have been deposited with the Editor].

Description and discussion of the structure

Bond lengths and angles, with estimated standard deviations in parentheses, are in Table V. Atomic numbering is E(NX) when E is the atom-type, N is the atom number and X is the ligand number (X = 1 to 4). Figure 2 contains a labelled diagram of the complexed cation, associated nitrate groups and the water molecule whose O-atom is labelled (99) to facilitate identification. H-atoms are numbered according to the heterocyclic atom to which they are attached.

The crystal structure consists of complexed cations, ionic nitrate groups and free water molecules held together by a combination of ionic, van der Waals' and H-bonded contacts.

The ligands are monodentate and S-bonded to the metal; the resultant, distorted, tetrahedral MS_4 unit is similar to others which have been reported in this series [12, 18]. Distortion of the tetrahedral cation produces S–Co–S angles ranging from 101.3(1)° to 126.0(1)° and non-bonded S····S contacts in the range 3.589 to 4.140 Å. The Co–S bond distances, (2.314(3) to 2.340(3) Å), are in the range quoted for Co–S, tetrahedral contacts (2.30(4) Å) [27] and compare with the value, 2.302(1) Å, found in $[Co(MImT)_4](ClO_4)_2$ [18]. The value expected from the sum of their covalent radii, 2.36(1) Å, [28]; and the averaged values observed for two of the forms of hydrated $Co(tu)_4(NO_3)_2$, namely, 2.305 Å [29] and 2.304 Å [30].

The dimensions of all four ligands are essentially the same and exhibit similar trends to those observed in related compounds of MImT [12, 18]. The C–S distances are relatively long (1.730(av) Å) and the

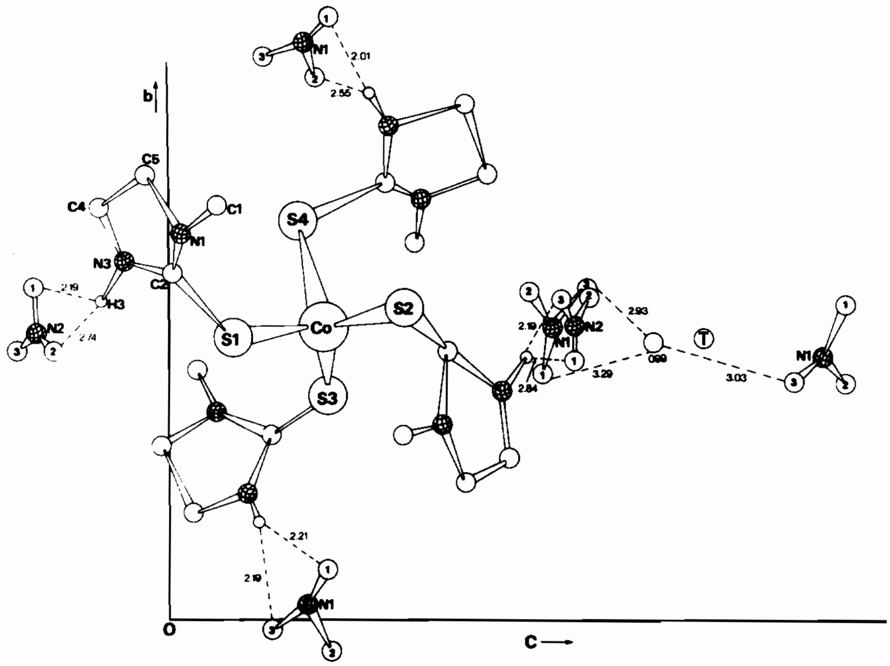

Fig. 2. Atomic-labelling and intermolecular contacts viewed down *a*. $\bar{1}$ is a centre of symmetry.

C–N distances involving the ethylenic C-atoms are longer than those within the thioamide portion of the ligand. Although the distances within the free ligand are not yet available, comparable values, for the exocyclic C–S distances in benzimidazoline-2-thione, 1.671(8) Å [31], and 1,3-dimethylimidazoline-2(3H)-thione, 1.696(5) Å [32], do support the observation that C–S distances do lengthen upon coordination of the S-atom to metals [33]. The range of Co–S(X)–C(2X) angles (101.6(4) to 105.4(4)°) supports the previously stated observation [12, 18], that the S atoms, in this series of structures are essentially tetrahedral in character.

The ligands are essentially planar with the largest deviation, from the least-squares mean planes, being 0.53 Å for C(42). Each ligand is twisted out of the related Co–S(X)–C(3X) plane with resultant dihedral angles ranging from 63.9° (X = 4) to 74.7° (X = 1); the range of values previously reported for this series of compounds is 66.0 to 77.2° [12, 18].

Extended chains of N–H····O contacts along *b* and *c* link the complexed cations to the nitrate groups; in addition, O–H····O contacts, along *c*, link the water molecules to centro-symmetrically related pairs of N(1)–O_3 groups. These relationships are shown in Fig. 2. Each of the O-atoms from the N(1)–O_3 group is H-bonded to the N–H group of either ligand 3 or 4. Thus the O(1) and O(3) atoms are joined to ligand 3 and the O(2) and O(1) atoms are joined to ligand 4. The H(33) atoms are symmetrically-bifurcated with short, strong H····O contacts. Similarly, the H(34) atoms are asymmetrically-bifurcated to the O(1) and O(2) atoms of the N(1)–O_3 group. In contrast to this behaviour only the O(1) and O(3) atoms of the N(2)–O_3 group form H-bonds, to ligands 1 and 2 respectively. The H····O distances observed for the O(1) and O(2)-atoms of the N(2)–O_3 group correspond to normal van der Waals' contacts. The water molecule is held in the lattice by O–H····O contacts to O(31) atoms from a pair of centro-symmetrically related N(1)–O_3 groups. Attempts to locate the H-atoms along the O(99)····O(31) vectors were unsuccessful due to the large degree of thermal motion of the O(99) atom.

Nitrate groups are effectively planar with dimensions in the range previously reported for such groups [34, 35].

Conclusions

The essentially monodentate, S-donating character of MImT, previously observed from a variety of M(II) ions [11–13, 18] has again been demonstrated.

Both the Co(II) and Zn(II) compounds of 1:4 stoichiometry are tetrahedrally coordinated by MImT; a similar structure is proposed for the Cd(II) compound. This confirms that the non-conducting nature of these compounds in nitromethane is anomalous and most likely arises as a result of ligand–nitrate exchange. A pseudo-tetrahedral structure is proposed for $Co(MImT)_2(NO_3)_2$, involving monodentate nitrate. The successful preparation of the latter compound is entirely dependent on the use of ethyl acetate as the solvent medium.

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