Co-ordination Chemistry of Thiomorpholin-3-one and Thiazolidine-2-thione. Complexes of some Bivalent Transition-metal Sulphates and Nitrates

By **Carlo Preti** * and **Giuseppe Tosi**, Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

Several complexes containing the ligands (L) thiomorpholin-3-one or thiazolidine-2-thione of general formula ML_nX_m are reported {M = Zn, Cd, Co, or Ni; X = $[SO_4]^{2-}$ (m = 1) and $[NO_3]^-$ (m = 2); n = 2, 4, or 6}. The complexes have been characterized by chemical analyses, ligand-field spectra, magnetic-susceptibility measurements, molecular conductance, and vibrational spectra (conventional and far infrared). Assignments for the metal–ligand modes have also been made. By use of i.r. spectroscopy it is possible to distinguish whether the anions present are co-ordinated to the transition metal ion or are present as free ions. Spectroscopic parameters for the cobalt and nickel complexes are compared with similar chromophores containing sulphur, oxygen, and nitrogen donor atoms. The evidence suggests that the zinc and cadmium complexes are tetrahedral, whereas the cobalt(II) and nickel(II) complexes are tetrahedral or octahedral.

STUDIES have been recently made[1] on the complex formation of sterically hindered heterocyclic ligands containing sulphur, nitrogen, oxygen, and selenium donor atoms with different metals in order to investigate the competitiveness of the different donor atoms in the co-ordination behaviour. These ligands behave as hard or soft bases depending on the metal ions employed.

We report here the preparation and characterization of thiomorpholin-3-one, $\overline{C(O)\cdot NH\cdot CH_2\cdot CH_2\cdot S\cdot CH_2}$ (tm), and thiazolidine-2-thione, $\overline{C(S)\cdot NH\cdot CH_2\cdot CH_2\cdot S}$ (tzt), complexes with zinc(II), cadmium(II), cobalt(II), and nickel(II) sulphates and nitrates for comparison purposes in order to further our present knowledge and to check the influence of the anion both on the co-ordination number of the metal, *i.e.* on the stereochemistry of the complex, and on the different co-ordination behaviour of the donor atoms of the ligands. These ligands contain three different reaction centres, namely cyclic nitrogen and sulphur atoms and the carbonyl oxygen in the case of tm, and cyclic nitrogen and sulphur atoms and the thiocarbonyl sulphur in the case of tzt.

RESULTS AND DISCUSSION

In Table 1 the co-ordination compounds obtained are reported together with analytical results, colours, melting points, and magnetic and conductivity values. The most important i.r. data are shown in Tables 2—5. The principal features of the visible absorption spectra of this series of complexes are given in Table 6. The complexes are microcrystalline, soluble in *NN*-dimethylformamide (dmf). All attempts to prepare mercury(II) derivatives with tm and tzt were unsuccessful because of the reduction of the metal by the ligands. The cobalt(II) and nickel(II) complexes have tetrahedral or octahedral stereochemistries.

As for the i.r. spectra, in the spectra of the complexes (Table 2) ν(NH) appeared as a broad band at 3 250—3 400 cm^{-1} compared with the value of 3 400 cm^{-1} for the free ligand tm in chloroform solution. The low value, 3 220 cm^{-1}, for ν(NH) of the spectrum of the solid free ligand arises from extensive hydrogen bonding which disappears on dissolution in chloroform. The ν(C=O) vibration occurred at 1 660 cm^{-1} in the spectrum of the free ligand and was shifted towards lower wavenumbers, 1 600—1 630 cm^{-1}, in the spectra of the complexes. The stretching vibrations due to ν(CS) (symmetric and asymmetric) occurred at the same wavenumbers or showed small positive shifts. These facts suggest that the donor site is the oxygen atom in the tm derivatives; in fact the carbonyl-stretching wavenumber is lowered by *ca.* 40 cm^{-1} whenever the oxygen atom is bonded to a metal.[2] The small negative shifts of ν(NH) in the spectra of these derivatives could arise from intermolecular hydrogen bonding.

For the complexes of thiazolidine-2-thione (tzt), the most important bands present in the i.r. spectra of the ligand and its complexes in the 60—4 000 cm^{-1} region are reported in Table 3. The ν(NH) band of the complexes was shifted negatively by *ca.* 250 cm^{-1} compared to the value of 3 400 cm^{-1} for the free ligand in chloroform solution; in Nujol mulls, this absorption occurs at

---

[1] C. Preti and G. Tosi, *Canad. J. Chem.*, 1975, **53**, 177 and refs. therein.

[2] S. C. Jain and R. Rivest, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2787.

TABLE 1

Analytical data and other physical properties

Compound	Colour	Analysis (%)								
		Found			Calc.					
		C	H	X [a]	C	H	X [a]	Λ [b] S cm^2 mol^{-1}	μ B.M.	Decomposition point (θ_c/°C)
$[Zn(tm)_2(SO_4)]$	White	24.4	3.5	16.2	24.3	3.6	16.1	10.60	*c*	70—72
$[Zn(tm)_4][NO_3]_2$	White	29.3	4.0	10.0	29.2	4.3	9.9	158.48	*c*	58—60
$[Cd(tm)_2(SO_4)]$	White	21.5	3.1	25.5	21.7	3.2	25.4	21.22	*c*	60—62
$[Cd(tm)_4][NO_3]_2$	White	26.8	3.7	15.9	27.2	4.0	15.9	186.31	*c*	62—64
$[Co(tm)_4(SO_4)]\cdot 2H_2O$	Pink-violet	29.3	5.1	8.6	29.1	4.9	8.5	10.61	4.6	78—80
$[Co(tm)_6][NO_3]_2\cdot H_2O$	Pink-violet	32.1	4.9	12.3	31.9	4.9	12.4	180.19	4.8	58—60
$[Ni(tm)_4(SO_4)]\cdot 4H_2O$	Green-yellow	27.5	5.3	7.6	27.6	5.2	8.0	7.60	3.2	70—72
$[Ni(tm)_6][NO_3]_2$	Green-yellow	32.8	4.8	12.5	32.5	4.8	12.6	160.41	2.9	58—60
$[Zn(tzt)(SO_4)]\cdot H_2O$	White	12.2	2.3	22.6	12.1	2.4	21.9	3.60	*c*	100—102
$[Zn(tzt)_2(SO_4)]$	White	18.1	2.5	16.4	18.0	2.5	16.4	3.86	*c*	103—105
$[Zn(tzt)_4][NO_3]_2$	White	21.6	3.2	9.9	21.6	3.0	9.8	185.27	*c*	83—85
$[Cd(tzt)_4][SO_4]$	White	21.1	2.3	16.4	21.0	2.3	16.4	52.61	*c*	130—132
$[Cd(tzt)_4][NO_3]_2$	White	20.3	2.8	15.9	20.2	2.8	15.8	142.98	*c*	55—57
$[Co(tzt)_4(SO_4)]$	Pink-violet	22.3	3.1	9.1	22.8	3.2	8.9	8.43	5.0	94—96
$[Co(tzt)_4][NO_3]_2\cdot 2H_2O$	Dark green	21.1	3.4	11.7	20.7	3.5	12.1	187.81	4.5	128—130
$[Ni(tzt)_4(SO_4)]\cdot 6H_2O$	Green-yellow	19.5	4.1	7.5	19.5	4.4	7.6	6.62	3.4	96—98
$[Ni(tzt)_2(NO_3)_2]$	Brown	17.0	2.4	13.2	17.1	2.4	13.3	15.85	3.5	>350

[a] Metal for the derivatives of Zn and Cd, nitrogen for those of Co and Ni. [b] For 10^{-3} mol dm^{-3} solutions in dmf. [c] Diamagnetic.

TABLE 2

Infrared absorption bands (cm^{-1}) of the tm derivatives

Compound	ν(NH)	ν(CO)	ν(CS) (sym., asym.)	Other bands
tm (solid)	3 220s	1 620s	692m, 643m	452s, 405vw, 350vw, 188s, 144s, 122m, 88 (sh), 71s
($CHCl_3$ solution)	3 400s	1 660vs	690m, 650m	
$[Zn(tm)_2(SO_4)]$	3 400s	1 620vs	690m, 650m	448mw, 412w, 337w, 188mw, 146m, 123m, 87 (sh), 69m
$[Zn(tm)_4][NO_3]_2$	3 390s	1 615vs	690m, 650m	470s, 410 (sh), 335mw, 198s, 144m, 114mw, 84w, 70m
$[Cd(tm)_2(SO_4)]$	3 250s	1 600s	700m, 650m	460s, 400 (sh), 340vw, 186m, 140m, 126w, 89 (sh), 68m
$[Cd(tm)_4][NO_3]_2$	3 290s	1 610s	690m, 650m	460s, 398vw, 342 (sh), 184m, 146ms, 120 (sh), 90 (sh), 70 m
$[Co(tm)_4(SO_4)]\cdot 2H_2O$	3 290s	1 620s	690m, 650m	460ms, 397vw, 345vw, 191m, 149m, 118 (sh), 72ms
$[Co(tm)_6][NO_3]_2\cdot H_2O$	3 290s	1 610s	695m, 650s	460s, 400vw, 357w, 187m, 150m, 115 (sh), 71ms
$[Ni(tm)_4(SO_4)]\cdot 4H_2O$	3 300s	1 630s	695ms, 650ms	460s, 408w, 349vw, 190m, 142w, 118w, 85 (sh), 66 (sh)
$[Ni(tm)_6][NO_3]_2$	3 310s	1 630s	695m, 650s	468s, 403w, 348vw, 191m, 146m, 125w, 88w, 71ms

TABLE 3

Infrared absorption bands (cm^{-1}) of the tzt derivatives

Compound	ν(NH)	Thioamide (I)	ν(C=S) + δ(NCS)	Thioamide (III)	ν(CS) (sym., asym.)	Other bands
tzt ($CHCl_3$ solution)	3 400s	1 490s	1 288vs	928s	690s, 650vs	434ms, 290m, 94m
$[Zn(tzt)(SO_4)]\cdot H_2O$	3 100s	1 490s	1 300s	932ms	680m, 640m	434ms, 290m, 96w
$[Zn(tzt)_2(SO_4)]$	3 140s	1 520s	1 305s	940ms	710m, 660m	431m, 291mw, 92w
$[Zn(tzt)_4][NO_3]_2$	3 115s	1 500s	1 300s	930s	700m, 650m	428ms, 291m, 91m
$[Cd(tzt)_4][SO_4]$	3 130s	1 520s	1 305s	935m	700m, 655m	429ms, 291m, 90 (sh)
$[Cd(tzt)_4][NO_3]_2$	3 000ms	1 500ms	1 300ms	930m	700m, 650m	431mw, 294m, 93mw
$[Co(tzt)_4(SO_4)]$	3 120ms	1 500vs	1 295vs	930ms	700ms, 660ms	433mw, 290m, 94vw
$[Co(tzt)_4][NO_3]_2\cdot 2H_2O$	3 190vs	1 520vs	1 310s	935m	700s, 660ms	426ms, 294mw, 92 (sh)
$[Ni(tzt)_4(SO_4)]\cdot 6H_2O$	3 130s	1 525vs	1 300s	937s	700s, 660ms	432mw, 293mw, 94w
$[Ni(tzt)_2(NO_3)_2]$	3 180s	1 525ms	1 315s	948m	695m, 650m	436mw, 294m, 96w

TABLE 4

		Absorption bands of nitrate group		
Compound	ν(M–L)	$\nu_2(A_2'')$	$\nu_3(E')$	$\nu_4(E')$
$[Zn(tm)_4][NO_3]_2$	505s, 365m	830s	1 380vs	730ms
$[Cd(tm)_4][NO_3]_2$	420ms, 358m	828s	1 390vs	715 (sh)
$[Co(tm)_6][NO_3]_2\cdot H_2O$	440s	832s	1 380vs	725m
$[Ni(tm)_6][NO_3]_2$	440s	830s	1 400vs	735s

			Absorption bands of sulphate group			
	ν(M–L)	ν(M–O)	ν_1	ν_2	ν_3	ν_4
$[Zn(tm)_2(SO_4)]$	500 (sh), 360m	260m, 237m		460ms	1 165ms, 1 130s, 1 055 (sh)	620m, 560m *
$[Cd(tm)_2(SO_4)]$	415ms, 360m	199m	995 (sh)	480w	1 165s, 1 125s, 1060mw	625m, 540m *
$[Co(tm)_4(SO_4)]\cdot 2H_2O$	420m	266m, 233m	990m	495m	1 165s, 1 130s, 1 055m	620m, 555m *
$[Ni(tm)_4(SO_4)]\cdot 4H_2O$	443m	264mw, 242m	990ms	510ms	1 150vs, 1 100vs, 1 050 (sh)	635ms, 570m

* Overlapping a ligand band which is markedly reinforced.

3 120 cm^{-1} and is very broad because of the presence of intermolecular hydrogen bonds. The band at 1 490 cm^{-1} assigned to thioamide (I),[3] having predominant C=N character, showed a positive shift; the same behaviour was observed for the band at 1 288 cm^{-1} assigned to ν(C=S) + δ(NCS), while the thioamide (III) showed a blue shift of *ca.* 20 cm^{-1}. The bands at 690 and 650 cm^{-1}, assigned to symmetrical and asymmetrical C–S stretching frequencies, showed positive shifts on co-ordination or remained at the same positions. The nitrogen atom is clearly the donor atom in the tzt derivatives because when a ligand is N-bonded, as in complexes of morpholine, thiazolidine-2-thione, thiomorpholine-3-thione, and thiazolidine-2-selenone, ν(NH) occurs as a sharp band at *ca.* 3 100 cm^{-1} with a shift of *ca.* 300 cm^{-1}.[4-9] The positive shifts of stretching vibrations due to bonds involving sulphur atoms suggest that these atoms are not involved in the co-ordination to the metals.

According to Singh and Rivest [9] a sharp NH band in the metal derivatives is indicative of absence of hydrogen bonding and a comparison of these values with the ν(NH) frequency of the ligand in solution could be used to suggest co-ordination through the nitrogen atom. Further evidence of this mode of co-ordination comes from the analysis of the thioamide bands; in fact thioamide (I) undergoes a blue shift and thioamide (III) shows similar behaviour, while in the case of a sulphur co-ordination it should have a marked red shift. The above conclusions are in accord with most of the observations on the previously reported complexes, and the electronic spectra provide further evidence on this point.

TABLE 5

Compound	ν(M–L)	ν(M–O)	Absorption bands of nitrate group				
			ν_1	ν_2	ν_3	ν_4	ν_6
$[Zn(tzt)_4][NO_3]_2$	165m			830ms (A_2'')	1 375vs (E')	785mw (E')	
$[Cd(tzt)_4][NO_3]_2$	172m			832mw (A_2'')	1 350vs (E')	740mw (E')	
$[Co(tzt)_4][NO_3]_2\cdot 2H_2O$	220m			830s (A_2'')	1 385vs (E')		
$[Ni(tzt)_2(NO_3)_2]$	219m	271m, 241m	1 260m (A_1)	985ms (A_1)	740w (A_1)	1 495m (B_1)	860m (B_2)
			Absorption bands of sulphate group				
	ν(M–L)	ν(M–O)	ν_1	ν_2	ν_3	ν_4	
$[Zn(tzt)(SO_4)]\cdot H_2O$	185s	267m, 240m	1 000s	465 (sh)	1 150s, 1 115s, 1 050s	590s, 550ms	
$[Zn(tzt)_2(SO_4)]$	187s	266m, 236m	1 002s	470m	1 155vs, 1 115s, 1 050s	620s, 585ms *	
$[Cd(tzt)_4][SO_4]$	180m				1 045vs	580s *	
$[Co(tzt)_4(SO_4)]$	219m	264m, 238m	1 000vs	465 (sh)	1 155vs, 1 095vs, 1 048s	635ms, 580ms *	
$[Ni(tzt)_4(SO_4)]$	218ms	263m, 239m	1 000s	480m	1 160ms, 1 100ms, 1 052vs	625mw, 588m *	

* Overlapping a ligand band which is markedly reinforced.

TABLE 6

Electronic spectra and ligand-field parameters (cm^{-1})

Compound	ν_3 $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	ν_2 $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	ν_1 * $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	*Dq*	*B'*	β
$[Co(tm)_4(SO_4)]\cdot 2H_2O$	20 575	16 530	7 700	883	934	0.97
$[Co(tm)_6][NO_3]_2\cdot H_2O$	20 410	16 805	7 835	897	914	0.95
$[Co(tzt)_4(SO_4)]$	20 835	16 670	7 760	891	948	0.98
	$^4A_2(F) \rightarrow {}^4T_1(P)$	$^4A_2(F) \rightarrow {}^4T_1(F)$	$^4A_2(F) \rightarrow {}^4T_2(F)$			
$[Co(tzt)_4][NO_3]_2\cdot 2H_2O$	14 815	7 635	4 500	450	597	0.62
	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$			
$[Ni(tm)_4(SO_4)]\cdot 4H_2O$	25 000	14 705	8 980	898	851	0.82
$[Ni(tm)_6][NO_3]_2$	24 815	14 925	9 200	920	809	0.78
$[Ni(tzt)_4(SO_4)]\cdot 6H_2O$	25 970	15 270	9 320	932	885	0.85
	$^3T_1(F) \rightarrow {}^3T_1(P)$	$^3T_1(F) \rightarrow {}^3A_2(F)$	$^3T_1(F) \rightarrow {}^3T_2(F)$			
$[Ni(tzt)_2(NO_3)_2]$	15 260	9 175	3 515	566	497	0.48

* Calculated values. *B* is taken to be 967 cm^{-1} for free Co^{2+} and 1 041 cm^{-1} for free Ni^{2+}.

As for the anions present in the complexes, by the use of i.r. spectroscopy it is possible to determine whether or not the anions are co-ordinated to the transition metals. Co-ordination lowers the original symmetry of the free ion and this is reflected in the number and intensity of its fundamental vibrations. The i.r. fundamental vibrational modes of the nitrato- and sulphato-groups are reported in Tables 4 and 5 respectively. In the nickel nitrato-derivative of tzt the symmetry is lowered from D_{3h} to C_{2v} indicative of a unidentate [10,11] and not a bidentate nitrato-group as the separation between the first two bands in the latter case is much larger.[12] The

---

[3] C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, 1962, **18**, 541.

[4] C. Preti and G. Tosi, *Canad. J. Chem.*, 1974, **52**, 2845 and refs. therein.

[5] G. Colombini and C. Preti, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1159.

[6] I. S. Ahuja, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2091.

[7] I. S. Ahuja and P. Rastogi, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 255.

[8] D. De Filippo, F. Devillanova, C. Preti, and G. Verani, *J. Chem. Soc.* (*A*), 1971, 1465.

[9] P. P. Singh and R. Rivest, *Canad. J. Chem.*, 1968, **46**, 2361.

[10] M. Choca, J. R. Ferraro, and K. Nakamoto, *J.C.S. Dalton*, 1972, 2297.

[11] M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.

[12] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1970.

difference between the ν_1 and ν_4 frequencies ($\Delta\nu$) has been used as a guide to the covalent nature of the nitrate group; the greater the difference, the more covalent the bonding. The difference $\Delta\nu$ of *ca.* 240 cm^{-1} in the nickel derivative is indicative of strong covalency in the metal–nitrate bond. Values of all the remaining nitrato-derivatives are typical of non-bonded nitrate. The conductivity values agree very well with these i.r. results; in fact all the complexes, except the tzt derivative of nickel, behave as 1 : 2 electrolytes in dmf.[13]

Passing to the sulphato-derivatives, in the complex $[Cd(tzt)_4][SO_4]$ the anion is not co-ordinated; in fact the SO_4 group belongs to the symmetry point group T_d and only the ν_3 and ν_4 bands were present in the i.r. spectrum (Table 5). In all the remaining complexes the symmetry is lowered and splitting of the degenerate modes occurs together with the appearance of new bands in the i.r. spectra corresponding to Raman-active bands in the free ion (Table 5). The lowering of symmetry, to C_{2v}, is typical of bidentate ligands. Some bands at 580—588 cm^{-1}, due to co-ordinated sulphato-groups, are believed to obscure a ligand band which is thereby reinforced. These conclusions are consistent with the conductivity measurements (Table 1) which show 1 : 1 electrolyte behaviour in dmf for the tzt derivative of cadmium, and non-electrolyte behaviour for all the other sulphato-complexes.[13]

The medium absorption bands present in the range 3 450—3 480 cm^{-1} [ν(OH)] and at 1 650 cm^{-1} [δ(HOH)] in all the water-containing complexes (Table 1) confirm the presence of water of crystallization. Evidence that this water is purely lattice water is given by the absence of the typical bands of co-ordinated water. In fact when water is co-ordinated to a metal, besides the three fundamental modes of the free molecule, other vibrational modes such as wagging, twisting, and rocking are activated.[14-17]

The conclusions regarding the co-ordination centre of the ligands, *i.e.* the oxygen atom of tm and the nitrogen atom of tzt, are in keeping with most of the observations on the complexes previously studied and reported, but we prefer to delay the question of the assignment of ν(M–L) until after the discussion of the electronic spectra.

Electronic Spectra.—Analysis of the electronic spectra of the cobalt(II) and nickel(II) derivatives allows us to determine the mode of bonding. With cobalt(II), complexes of octahedral and tetrahedral geometries are formed. Their magnetic moments and solid-state electronic spectra (Tables 1 and 6) are in accord with those expected for these stereochemistries. For the octahedral derivatives of Co^{II}, the Dq, B', and β parameters were evaluated using ν_2 and ν_3.[18] The wavenumber of ν_1 was not identified from the experiments because in the spectrum of the free ligand tm a medium–strong absorption is present at 8 300 cm^{-1} and an unambiguous assignment was not possible in the tzt complexes. Calculated ν_1 values are in Table 6. The complex $[Co(tzt)_4][NO_3]_2\cdot 2H_2O$ had a magnetic moment of 4.5 B.M.* at room temperature and an electronic spectrum consistent with a tetrahedral configuration for high-spin cobalt(II) (Tables 1 and 6). Using the frequencies of ν_2 and ν_3, we calculated the values of the crystal-field parameters.[18] The value of B' suggests considerable orbital overlap. Passing to the nickel(II) derivatives, all the complexes are octahedral with the exception of $[Ni(tzt)_2(NO_3)_2]$ which, like the analogous cobalt derivative, is tetrahedral. The magnetic-moment measurements and solid-state electronic spectra are in very good agreement with these results. The values of Dq, B', and β were calculated from only ν_2 and ν_3. The B' values, of about the same order of magnitude as the cobalt derivatives, suggest strong covalency in the metal–ligand σ bond.

By comparison with Dq values reported for $[CoL_4]^{2+}$ cations,[19] we can see that for CoS_4 chromophores Dq lies in the range 316—425 cm^{-1}; the corresponding range for CoN_4 chromophores is 447—538 cm^{-1}. Table 6 shows that the Dq value of the complex $[Co(tzt)_4][NO_3]_2\cdot 2H_2O$ is in very good agreement with the literature data for CoN_4 chromophores. For $[CoL_6]^{2+}$ cations, the Dq values for CoS_6 chromophores are in the range 770—860 cm^{-1}, for CoO_6 in the range 920—980 cm^{-1}, while the values corresponding to CoN_6 chromophores are higher than 1 000 cm^{-1}.[20,21] The Dq values of the tm derivatives of cobalt agree very well with the data for $[CoL_6]^{2+}$ complexes containing cobalt–oxygen bonds. The complex $[Co(tzt)_4(SO_4)]$ shows a Dq value that is, using the 'law of the average environment', typical of CoN_4O_2 chromophores. This value is obviously lower than those of $[CoN_6]^{2+}$ complexes. For the octahedral nickel(II) derivatives the Dq values for NiS_6 and NiO_6 chromophores lie between 770 and 810 cm^{-1} and 850 and 930 cm^{-1} respectively, higher values being expected for NiN_6 groups.[20,21] The tm derivatives have Dq values in accord with the reported data for $[NiO_6]^{2+}$ cations, while the complex $[Ni(tzt)_4(SO_4)]\cdot 6H_2O$ shows a value typical of NiN_4O_2 chromophores. Comparison of the electronic spectrum of the complex $[Ni(tzt)_2(NO_3)_2]$ with those of derivatives having Ni–N and Ni–S bonds confirms that the complex is N-bonded, the band energies being at higher values than for S-bonded derivatives.[20,22]

These results strongly support the i.r. conclusions that the tm derivatives are O-bonded while the tzt complexes are N-bonded.

---

* 1 B.M. $\approx 9.27 \times 10^{-24}$ Am^2.

[13] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[14] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.

[15] I. Gamo, *Bull. Chem. Soc. Japan*, 1961, **34**, 760, 764, 1430, 1433.

[16] G. Sartori, C. Furlani, and A. Damiani, *J. Inorg. Nuclear Chem.*, 1958, **8**, 119.

[17] C. Preti and G. Tosi, *Spectrochim. Acta*, 1975, **A31**, 1139.

[18] A. E. Underhill and D. E. Billing, *Nature*, 1966, **210**, 834.

[19] B. P. Kennedy and A. B. P. Lever, *Canad. J. Chem.*, 1972, **50**, 3488.

[20] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.

[21] C. K. Jorgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, Oxford, 1962.

[22] C. Preti, G. Tosi, D. De Filippo, and G. Verani, *Canad. J. Chem.*, 1974, **52**, 2021.

Far-infrared Spectra.—It is interesting that the direction of the shifts in positions of all the bands of the ligands is the same. This clearly indicates that the bonding pattern must be similar in the cobalt and nickel and in the zinc and cadmium derivatives. In Table 4 are reported the vibrational modes due to the metal–oxygen interaction of the tm complexes.[1,5,8] In the tzt derivatives the co-ordination centre is the nitrogen atom; the ν(M–N) stretching modes are in Table 5, and are in very good agreement with previously reported data for similar complexes.[1,5,8]

The low-frequency i.r. spectra of all the new complexes involving co-ordinated nitrato-groups exhibited bands attributable to ν(M–O) nitrate modes; [23–25] tentative assignments are given in Table 5. The spectra of all the metal sulphate complexes, except $[Cd(tzt)_4][SO_4]$, showed medium absorption bands, either one or two in the range 199—274 cm^{-1}. Since such bands were not observed in the spectra of the corresponding halide derivatives, these could be considered as due to metal–oxygen modes of the co-ordinated anion.

Conclusions.—In order to determine the position of the present ligands in the spectrochemical series, the *Dq* values of the complexes were compared with those of known tetrahedral and octahedral cobalt(II) derivatives. For the tetrahedral cobalt(II) derivatives the following order for the ligands is suggested: thiomorpholine > morpholine > benzothiazole > benzoxazole-2-thione > 2-methylbenzimidazole > 3-methyl-5-phenylisoxazole > isoxazole > 2-aminobenzimidazole > thiomorpholine-3-thione > thiazolidine-2-thione > 3,5-dimethylisoxazole > thiazolidine-2-selenone > ε-thiocapro-lactam > triphenylarsine oxide ≈ triphenylphosphine oxide > dimethylacetamide. Passing to Co^{II} in an octahedral geometry the ligands could be placed in the spectrochemical series as follows: imidazole > piperidine > ammonia ≈ pyridine *N*-oxide > 4-methylpyridine *N*-oxide > 3-methyl-5-phenylisoxazole > 3,5-dimethylisoxazole > benzeneseleninic acids > water > thiomorpholin-3-one (O-bonded) > dimethyl sulphoxide > thiazole > thiomorpholin-3-one (S-bonded).

The ligand tm behaves as a hard or soft base through the oxygen or sulphur atom. With this ligand we have never obtained complexes in which the co-ordination centre is the nitrogen atom.[1,4] Furthermore, the cobalt(II) and nickel(II) derivatives which resulted were always of the type $[ML_6]^{2+}$ with the metal atom in an octahedral stereochemistry, both with halides and different anions such as perchlorates, tetrafluoroborates, sulphates, and nitrates. With a Group 2B metal, complexes with a 1 : 1 or 1 : 2 metal : ligand ratio have been obtained with halides and other anions.[1] In the case of the tzt derivatives, six- or four-co-ordinate complexes have been prepared independently with the anion used in the cases of the cobalt(II) and nickel(II) complexes. For Group 2B metals it was possible to obtain complexes with a metal : ligand ratio of 1 : 1 or 1 : 2, but with thiocyanate acetate, and tetrafluoroborate ions [5] we always obtained 1 : 2 complexes. In this study we have obtained 1 : 2 or 1 : 4 complexes, with the exception of $[Zn(tzt)(SO_4)]\cdot H_2O$.

The reducing properties of the ligands are stronger in the presence of the polyanions than in the case of the halides. In fact, we have not been able to prepare complexes of mercury thiocyanate with tzt or of mercury acetate, nitrate, and sulphate with tm and tzt because of rapid reduction of Hg^{II} to Hg^{0}.

The ligand tzt can use all three of its heteroatoms as donors, but we have never obtained complexes in which the ligand is bidentate in monomeric or polymeric derivatives. The same behaviour is shown by thiomorpholin-3-one.

EXPERIMENTAL

Purification of the Ligands.—Thiomorpholin-3-one, (tm), supplied by Aldrich, was purified by extraction with diethyl ether in a Soxhlet apparatus (m.p. 93, lit.[26] 93 °C). Thiazolidine-2-thione (tzt), supplied by Fluka, was recrystallized twice from hot water (m.p. 106—107, lit.[27] 106—107 °C).

Preparation of the Complexes.—All the complexes were prepared by reaction of the corresponding metal salts with a small excess of the molten ligands. The complexes were purified by repeated washing with diethyl ether (tm derivatives) or with toluene (tzt derivatives).

Physical Measurements.—I.r. spectra were recorded in the range 60—4 000 cm^{-1} with Perkin-Elmer 457 and 225 and Hitachi–Perkin-Elmer FIS3 spectrophotometers. The spectra in the range 400—4 000 cm^{-1} were measured on KBr discs. Far-i.r. spectra were recorded as Nujol mulls supported between polyethylene sheets. Solid-state electronic spectra were obtained with a Shimadzu MPS-50L spectrophotometer using the method of Dyer et al.[28] Magnetic-susceptibility measurements were made by the Gouy method. Molecular susceptibilities were corrected for the diamagnetism of the component atoms by use of Pascal constants. Conductivity measurements were made with a type WTW LBR conductivity bridge on 10^{-3} mol dm^{-3} solutions in *NN*-dimethylformamide at 25 °C.

We thank Dr. G. Razzoli for his experimental work, Mr. G. Pistoni for elemental analyses, and the National Research Council (C.N.R.) of Italy for support.

[5/1818 *Received, 22nd September*, 1975]

---

[23] J. R. Ferraro and A. Walker, *J. Chem. Phys.*, 1965, **42**, 1273, 1278.

[24] R. H. Nuttall and D. W. Taylor, *Chem. Comm.*, 1968, 1417.

[25] J. I. Bullock and F. W. Parrett, *Chem. Comm.*, 1969, 157.

[26] A. H. Sommers and B. W. Horrom, *J. Amer. Chem. Soc.*, 1954, **76**, 1187.

[27] Handbook of Chemistry and Physics, 49th edn., ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 1968—1969, p. C565.

[28] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.