Inorganica Chimica Acta, 43 (1980) 73–76

Formation and Spectral Characterisation of N,N′-disubstituted-Oxamide [$\underline{O}\,\underline{O}$], -Thiooxamide [$\underline{S}\,\underline{S}$] and -Malonamide [$\underline{O}\,\underline{O}$] Complexes with Titanium(IV) and Tin(IV) Chlorides

S. R. WADE and G. R. WILLEY

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, U.K.

Received April 23, 1980

Several complexes of the type $MCl_4 \cdot B$ [M = Ti, Sn; B = N,N′-dimethyloxamide (DMO), N,N′-dimethylmalonamide (DEM), N,N′-dimethyldithiooxamide (DMDTO), N,N′-diethyldithiooxamide (DEDTO); M = Ti, B = N,N′-diethyloxamide (DEO)] have been prepared and characterised. Consideration of their IR and NMR spectral data allows an evaluation of the type of ligand attachment. In each case chelation involving either [$\underline{O}\,\underline{O}$] or the corresponding [$\underline{S}\,\underline{S}$] coordination to the metal is discussed. The complexes are covalent. Where direct comparison is possible it appears that the $\underline{S}$ donors are more strongly bonded to the metal than the corresponding $\underline{O}$ donors.

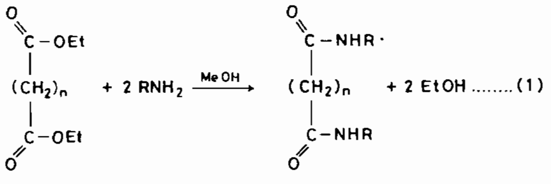
Introduction

Diamides (θ = $\underline{O}$) and dithioamides (θ = $\underline{S}$) and their N-substituted derivatives $RR'N(\theta)C{-}(CH_2)_n{-}C(\theta)NRR'$ readily form metal complexes. Typical examples include *I*: M = Ni(II); θ = $\underline{S}$; n = 0; R = R′ = H; R = H,R′ = Me [1]; *II*: M = Sb(III), Bi(III); θ = $\underline{S}$; n = 1; R = R′ = H; R = H, R′ = Me; R = H, R′ = C_6H_5 [2]; *III*: M = Pd(II); θ = $\underline{S}$; n = 1; R = Me, R′ = Me; R = H, R′ = H [3]; *IV*: M = Sb(III); θ = $\underline{S}$; n = 0; R = H, R′ = Et [4]. With no X-ray structural data available for such complexes, inferences in favour of either sulfur (oxygen) and/or nitrogen donation rely almost exclusively on IR evidence. Shifts in characteristic thioamide bands appear sensitive to the electronic and steric changes implicit with metal–ligand bonding [5, 6]. Structural studies of the ligands oxamide [7], dithiooxamide [8], succinamide [9] and N,N-dimethyldithiooxamide [10] show that there is extensive delocalisation within NCO(S) moieties but not along the carbon–carbon skeleton between them; bond angles ~120° around N support trigonal planar hybridisation. Also hydrogen bonding inter/intra is present to varying extents in the solid phase. N,N-dimethyldithiooxamide, unlike the parent dithiooxamide, is not planar and has a dihedral angle SCCS = 91.8° perhaps the direct result of reduced H-bonding. Without an accompanying geometry change $sp^2 \rightarrow sp^3$ or, better still, deprotonation to generate a formal lone pair at the N sites, a relative donor ability S(O) > N might be expected. This is seemingly borne out by the predominance of bidentate [$\underline{O}\,\underline{O}$] and [$\underline{S}\,\underline{S}$] ligand-metal binding; the 'mixed' [$\underline{S}\,\underline{N}$] donation proposed for the Ni(II)–dithiooxamide complexes I [1] has incipient proton loss. We can find no examples for the 'mixed' [$\underline{O}\,\underline{N}$] type in the literature.

In this study we consider the relative donor order ($\underline{O}$) ~ ($\underline{S}$) ~ ($\underline{N}$) within a representative set of N,N′-disubstituted-oxamide-thiooxamide, and -malonamide ligands using titanium(IV) and tin(IV) chlorides as reference Lewis acids.

Experimental

All manipulations involving the metal complexes were carried out in a gloved-box flushed with dry, oxygen-free nitrogen. Solvents (Analar) were stored over CaH_2/P_2O_5 and distilled under nitrogen prior to use. $TiCl_4$ and $SnCl_4$ were used as supplied commercially. The diamide ligands were prepared by treatment of the appropriate ethyl ester with either 25% aqueous $MeNH_2$ or anhydrous $EtNH_2$ in methanol solutions, eqn. (1).



$$EtO{-}C(O){-}(CH_2)_n{-}C(O){-}OEt + 2\,RNH_2 \xrightarrow{MeOH} RHN{-}C(O){-}(CH_2)_n{-}C(O){-}NHR + 2\,EtOH \quad (1)$$

(a) n = 0, R = Me(DMO) R = Et(DEO)
(b) n = 1 R = Et(DEM)

Where necessary, the white semi-crystalline products were recrystallised from $MeOH/EtOH/Et_2O$ solutions. N,N′-dimethyldithiooxamide (DMDTO)

TABLE I. Analytical Data of $MCl_4 \cdot B$ Complexes.

	mp[a]	Colour	Λ_M[b]	%C		%H		%N		%Cl	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$TiCl_4 \cdot$DMO	>543	yellow	0.93	15.7	15.7	2.6	2.8	9.2	9.1	46.4	45.9
$SnCl_4$:DMO	>524	white	0.77	12.8	13.0	2.2	2.2	7.4	7.6	37.7	37.6
$TiCl_4 \cdot$DEO	>493	yellow	1.41	21.6	21.7	3.6	3.8	8.4	8.4	42.4	41.1
$TiCl_4 \cdot$DEM	>419	pale yellow	0.09	24.2	24.0	4.1	4.0	8.1	7.9	40.8	40.1
$SnCl_4 \cdot$DEM	>473	white	0.44	20.1	20.0	3.4	3.4	6.7	6.5	33.8	32.8
$TiCl_4 \cdot$DMDTO	>458	orange	1.07	14.2	14.6	2.4	2.7	8.3	7.9	42.0	41.7
$SnCl_4 \cdot$DMDTO	>466	pale yellow	1.31	11.8	12.0	2.0	2.1	6.9	6.9	34.7	34.1
$TiCl_4 \cdot$DEDTO	>413	orange	0.66	19.7	19.9	3.3	3.3	7.7	7.9	38.7	38.3
$SnCl_4 \cdot$DEDTO	>458	pale yellow	0.82	16.5	16.1	2.8	3.1	6.5	6.3	32.5	31.8

[a] Melting with decomposition, (K) uncorrected. [b] (Ω^{-1} mol^{-1} cm^2) in 10^{-3} M solutions in CH_3NO_2.

TABLE II. Principal IR Bands (cm^{-1}) of $MCl_4 \cdot B$ Complexes.[a]

	ν(NH)	Thioamide I ν(CN)	Thioamide IV ν(CS)	ν(CO)	ν(MCl)
DMO	3300 (s)	1522 (s, br)		1655 (s, br)	
$TiCl_4 \cdot$DMO	3320 (w) 3270 (s) 3220 (m) 3150 (vs)	1578 (m)		1631 (s, br)	368 (vs, br) 303 (m) 276 (w)
$SnCl_4 \cdot$DMO	3325 (w) 3288 (s) 3217 (w) 3150 (m)	1571 (m)		1635 (s, br)	345 (vs, br) 285 (m)
DEO	3290 (vs)	1518 (s)		1650 (vs)	
$TiCl_4 \cdot$DEO	3310 (w) 3260 (s) 3202 (m) 3135 (s)	1572 (s)		1632 (vs, br)	355 (vs, br) 312 (w) 290 (w)
DEM	3292 (vs)	1550 (s, br)		1645 (s, br)	
$TiCl_4 \cdot$DEM	3295 (vs)	1575 (m, br)		1630 (vs, br)	340 (vs, br) 273 (m)
$SnCl_4 \cdot$DEM	3370 (sh) 3340 (sh) 3300 (vs)	1574 (m, br)		1628 (s, br)	323 (vs, br) 295 (w)
DMDTO	3169 (vs)	1529 (s, br)	870 (vs)		
$TiCl_4 \cdot$DMDTO	3225 (vs)	1564 (vs, br)	770 (s)		370 (vs, br) 342 (w) 305 (w)
$SnCl_4 \cdot$DMDTO	3198 (s)	1568 (s)	792 (s)		315 (vs, br)
DEDTO	3186 (s)	1518 (vs)	842 (s)		
$TiCl_4 \cdot$DEDTO	3260 (s) 3190 (s) 3096 (m)	1572 (vs)	800 (m)		360 (s, br) 285 (w)
$SnCl_4 \cdot$DEDTO	3210 (vs) 3098 (s)	1570 (vs)	793 (s)		310–320 (vs, br)

[a] Solid state (mull) spectra; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

and N,N'-diethyldithiooxamide (DEDTO) were prepared by reaction of the corresponding oxo-species with P_4S_{10} using a modified route to that of Hurd *et al.* [11] as described previously [4]. The metal complexes were prepared by direct addition of MCl_4 (M = Ti and Sn) to the appropriate ligand. In a typical reaction, $TiCl_4$ (1 cm^3, 9.1 mmol) dissolved in benzene (20 cm^3) was added dropwise to a stirred solution of DEDTO (1.6 g, 9.1 mmol) in 100 cm^3 of benzene. An orange, semi-crystalline solid slowly

TABLE III. ^{1}H and ^{13}C NMR Data for MCl$_4$·B Complexes.

	^{1}H†					^{13}C‡				
	$N{-}\underline{CH_3}$	$N{-}\underline{H}$	$N{-}\underline{CH_2}{-}$	$N{-}CH_2{-}\underline{CH_3}$	$-(\underline{CH_2})_n-$	$N{-}CH_3$	$N{-}CH_2$	$N{-}CH_2{-}CH_3$	$\overset{\diagdown\;\diagup}{\underset{\mid}{C}}$	$-(CH_2)_n-$
DMO	2.83(a)	7.59(b)				26.39^y			162.36^y	
TiCl$_4$·DMO	3.26(c)	9.12(b)								
SnCl$_4$·DMO	3.32(a)	8.80(b)								
DEO		7.71(b)	3.30(e)	1.15(d)			35.36	14.69	161.64	
TiCl$_4$·DEO		8.86(b)	3.74(e)	1.39(d)						
DEM		6.99(b)	3.21(e)	1.09(d)	3.40(f)		34.45	14.43	167.75	43.09
TiCl$_4$·DEM		7.66(b)	3.49(e)	1.27(d)	3.88(f)					
SnCl$_4$·DEM		7.97(b)	3.52(e)	1.27(d)	4.02(f)					
DMDTO	3.27(a)	10.39(b)				34.12^y			132.53^y	
TiCl$_4$·DMDTO	3.40(c)	9.96(b)								
SnCl$_4$·DMDTO	3.33(c)	10.28(b)								
DEDTO		10.35(b)	3.74(e)	1.33(d)			42.38	12.61	184.33	
TiCl$_4$·DEDTO		10.29(b)	3.76(g)	1.34(d)						
SnCl$_4$·DEDTO		10.00(b)	3.91(g)	1.45(d)						

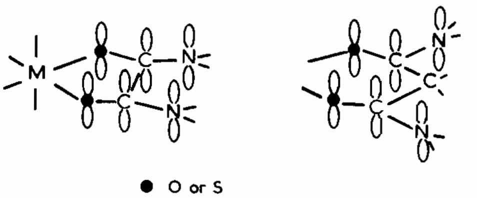
† δ (ppm) of CD$_3$NO$_2$ solutions downfield from internal TMS (δ = 0); ‡ δ (ppm) downfield from internal TMS using CDCl$_3$ solutions: (a) doublet, (b) broad singlet, (c) poorly resolved doublet, (d) triplet, (e) two superposed quartets as pseudo-pentaplet, (f) sharp singlet, (g) poorly resolved pseudo-pentaplet; ^{y}using CD$_3$OD solutions.

deposited. This was collected, washed with benzene and n-hexane and dried *in vacuo* at room temperature (Yield 3.1 g, 94%). Microanalysis results are listed in Table I.

IR spectra were recorded on a Perkin-Elmer 621 spectrophotometer with samples held as nujol and fluorolube mulls between CsI plates. Conductivity measurements were carried out with a Wayne-Kerr Universal B221 conductance bridge and a cell of standard design previously calibrated with aqueous KCl solutions. ^{1}H and ^{13}C NMR spectra were recorded as CD$_3$NO$_2$ solutions using Brüker WH90 (90 MHz) and Perkin-Elmer R 34 (220 MHz) spectrometers.

Discussion

The metal complexes are listed in Table I. All are extremely air-moisture sensitive and, excepting a limited solubility in nitromethane do not readily dissolve in the common organic solvents. Solutions in nitromethane are non-conducting. Principal IR bands are presented in Table II with assignments following those of Dessyn and Herman [5, 6]. For the diamides the low energy shift of the ν(CO) band and the accompanying high energy shift of ν(CN) support metal–oxygen [$\underline{O}\,\underline{O}$] bonding. Equally the decrease of ν(CS) and a similar increase of ν(CN) indicates metal–sulphur [S S] bonding in the dithioamides. A *cis*-octahedral structure (C_{2v}) is proposed



A single intense ν(NH) band is retained in several cases *e.g.*, TiCl$_4$·DEM, TiCl$_4$·DMDTO and SnCl$_4$·DMDTO with a slight increase in frequency: the remainder show multiplet ν(NH) bands attributed to solid state/lattice effects. Once the ligand is 'frozen' into a *cis*oid configuration by complexation it is an open question whether delocalisation now includes the C–C skeleton. Certainly the six-membered malonamide complexes are unlikely to show co-planarity. Strong multiple ν(MCl) bands in the 400–250 cm^{-1} region correlate with a *cis*-octahedral (C_{2v}) metal geometry.

Previous assignment of ($\underline{N}\,\underline{N}$) chelation for several unsubstituted dithiooxamide complexes with Group IV halides rests on ν(NH) variations, within the range (–90 → +50) cm^{-1}, and a positive shift of a band at 1430 cm^{-1} assigned as a ν(CS) mode [12]. The latter has been reinterpreted as the thioamide II band mainly due to δ(NH). A low energy shift for

ν(NH) by some 100–200 cm^{-1} is typical for amine coordination.

^1H NMR data is listed in Table III. Considering first the ligands: the methyl-substituted derivatives show (CH_3) doublets as a result of spin–spin splitting by the amide proton (NH spin decoupling gives the expected singlet). For the ethyl-substituted series, two superimposed quartets (pseudo-pentaplet)(CH_2) and a triplet (CH_3) are observed (a clearly resolved quartet and triplet are produced on NH spin decoupling). The NH proton appears as a broad singlet throughout. No splitting was noted for the bridging CH_2 in the malonamide species. Retention of these patterns at low temperatures (~200 K) signifies free rotation about the C–C skeleton with minimal H-bonding in solution.

On complex formation there is a general shift to low field for all resonances. Multiplet patterns persist *e.g.*, $TiCl_4 \cdot DEO$ δ_{NH} 7.71 → 8.86 (broad singlet); δ_{CH_2} 3.30 → 3.74 (pseudo-pentaplet) and δ_{CH_3} 1.15 → 1.39 (triplet). These must originate from spin–spin splitting and cannot be taken as evidence for the presence of geometrical isomers in solution as suggested earlier in the case of $SbCl_3 \cdot (DEDTO)_{1.5} \cdot (C_2H_4Cl_2)$ [4]. Although the observed increase in the double bond character of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ linkage must affect the free rotation of that bond, it is insufficient to force non-equivalence (magnetic) of the NHR groups in solution. On average chemical shifts are considerably greater for $[\underline{O}\,\underline{O}]$ complexes *e.g.*, $SnCl_4 \cdot DMO$ δ_{CH_3} 2.83 → 3.32, δ_{NH} 7.59 → 8.80, than for the corresponding $[\underline{S}\,\underline{S}]$ complexes *e.g.*, $SnCl_4 \cdot DMDTO$ δ_{CH_3} 3.27 → 3.33, δ_{NH} 10.39 → 10.28. For any one ligand, either oxo- or thio- species, there is no significant variation in chemical shift between the Ti(IV) and the corresponding Sn(IV) complexes, *e.g.*, $TiCl_4 \cdot DMO$, δ_{CH_3} 3.26, δ_{NH} 9.12: $SnCl_4 \cdot DMO$ δ_{CH_3} 3.32, δ_{NH} 8.80. This observed relative order $[\underline{O}\,\underline{O}] > [\underline{S}\,\underline{S}]$ for net electron transfer NHR → π-N-CO(S) correlates with the IR data where variations in the thioamide band I – as indicator of the double bond character of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond – are marginally greater for the $[\underline{O}\,\underline{O}]$ than for the $[\underline{S}\,\underline{S}]$ complexes. Consequently the low energy shifts of the ν(CO), 17–24 cm^{-1} and the ν(CS), 47–100 cm^{-1} bands directly reflect the relative donor capacity of the two ligand sets *i.e.*, the $\underline{S}$-donors are more strongly bound to the metal than the corresponding $\underline{O}$-donors. Though Ti(IV) and Sn(IV) are generally regarded as 'hard' (class A) and 'borderline' (class A ~ class B) Lewis acids respectively [13], there is plenty of evidence to suggest that sulphur is often a more effective donor than oxygen certainly for MCl_4 (M = Ti, Zr and Hf) [14].

^{13}C NMR data is unavailable for the metal complexes due to their limited solubility. Ligand resonances are included in Table III for reference.

Acknowledgments

We are grateful to Mlle Catherine Mabillard and David Rylance for experimental assistance and to the S.R.C. for a studentship award (to S.R. Wade).

References

1 G. Peyronel, G. C. Pellacani and A. Pignedoli, *Inorg. Chim. Acta, 5,* 627 (1971).

2 G. C. Pellacani, G. Peyronel, W. Malavasi and L. Menabue, *J. Inorg. Nucl. Chem., 39,* 1855 (1977).

3 A. J. Aarts, H. O. Desseyn and M. A. Herman, *Inorg. Chim. Acta, 29,* L197 (1978).

4 S. O. Wandiga, L. S. Jenkins and G. R. Willey, *J. Inorg. Nucl. Chem., 41,* 941 (1979).

5 H. O. Desseyn and M. A. Herman, *Spectrochim. Acta, 23A,* 2457 (1967).

6 H. O. Desseyn, W. A. Jacob and M. A. Herman, *Spectrochim. Acta, 25A,* 1685 (1969).

7 E. M. Ayerst and J. R. C. Dukes, *Acta Cryst., 7,* 588 (1954).

8 B. Long, P. Markey and P. J. Wheatley, *Acta Cryst., 7,* 140 (1954); P. J. Wheatley, *J. Chem. Soc.,* 396 (1956).

9 D. D. Daviel and R. A. Pasternak, *Acta Cryst., 9,* 334 (1956).

10 A. Christensen, H. J. Geise and B. J. Vandor Veken, *Bull. Chem. Soc. Belg., 84,* 1173 (1975).

11 R. N. Hurd, G. de la Mater, G. C. McElheny, R. J. Turner and V. H. Wallingford, *J. Org. Chem., 26,* 3980 (1961).

12 S. C. Jain and R. Rivest, *J. Inorg. Nucl. Chem., 29,* 2787 (1967).

13 S. Ahrland, *Struct. and Bonding, 1,* 207 (1966); *ibid., 5,* 118 (1968).

14 See *e.g.*, G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.,* 4330 (1964).
F. M. Chung and A. D. Westland, *Canad. J. Chem., 47,* 195 (1969); *ibid., 48,* 2871 (1970).
B. Hessett and P. G. Perkins, *J. Chem. Soc. (A),* 3229 (1970).
K. Baker and G. W. A. Fowles, *J. Less-Common Metals, 8,* 47 (1965).