Tetramethylenedithiocarbamates of the Early Transition Metals

By **T. M. Brown** * and **J. N. Smith**, Arizona State University, Tempe, Arizona 85281, U.S.A.

Tetrakistetramethylenedithiocarbamatometals $M[S_2CN(CH_2)_4]_4$ (M = Nb^{IV}, Mo^{IV}, and W^{IV}) have been prepared by reactions of ammonium tetramethylenedithiocarbamate and the respective metal tetrachloride in acetonitrile. The pentakis-compound $Ta[S_2CN(CH_2)_4]_5$ was also prepared. Spectroscopic (u.v., visible, and i.r.) and magnetic susceptibility studies were carried out on the compounds. The niobium, molybdenum, and tungsten compounds appear to be eight-co-ordinate.

NN-DIALKYLDITHIOCARBAMATE complexes have been recently reported for niobium,[1-3] tantalum,[1,2] molybdenum,[4] and tungsten.[2] The method used for the preparation of these compounds utilized the addition of carbon disulphide to the metal dialkylamides.[1,4] The synthesis of these compounds is more conveniently carried out by reacting the metal chlorides with sodium *NN*-dialkyldithiocarbamate in acetonitrile.[2] This method also allows for the preparation of the tungsten derivative for which no tungsten(IV) dialkylamide is known, and for a more direct route to the tetramethylenedithiocarbamates and other related compounds. The

$$MCl_4 + 4NH_4S_2CN(CH_2)_4 \xrightarrow{CH_3CN} M[S_2CN(CH_2)_4]_4 + 4NH_4Cl$$

need for the highly reactive metal dialkylamides is also avoided. These compounds were of interest in view of the lack of information on compounds of these elements having a co-ordination number greater than six.

Although niobium(V) undergoes reduction to the (4+) oxidation state, and it is reasonable to suspect that molybdenum(V) and tungsten(V) would do likewise, tantalum(V) forms the stable pentakistetramethylenedithiocarbamate. These results are similar to those observed with *NN*-dithiocarbamate. Tantalum(IV) is not sufficiently stable in acetonitrile to allow for the preparation of the tantalum(IV) derivative. Some of the properties of the tetramethylenedithiocarbamates are listed in the Table.

Analytical and physical data

Compound	Decomp. point (°C)	Colour	Analysis							
			Calc. (%)				Found (%)			
			C	H	N	S	C	H	N	S
$Mo(S_2CN[CH_2]_4)_4$	235	Rust brown	35·3	4·7	8·25	37·65	35·0	4·55	8·05	37·35
$W(S_2CN[CH_2]_4)_4$	70	Dark brown	31·2	4·15	7·3	33·35	31·2	4·25	7·55	33·05
$Nb(S_2CN[CH_2]_4)_4$	130	Purple	35·4	4·7	8·25	37·85	35·25	4·65	8·1	37·55
$Ta(S_2CN[CH_2]_4)_5$	220	Yellow	32·9	4·4	7·65	35·05	32·7	4·55	7·55	34·9

Compound	Infrared spectra (cm^{-1})				Magnetic moment μ_{eff} (B.M.)	Electronic absorption spectra (kK)
	C–N band	NC_2 band	C–S band	M–S band		
$Mo(S_2CN[CH_2]_4)_4$	1490	1166	1012	335	2·11; $\theta = -9°$	41·3, 38·2sh, 37·0, 28·2, 22·2, 21·3sh, 18·9
$W(S_2CN[CH_2]_4)_4$	1520	1168	1009	346	0·98; $\theta = -42$	39·2sh, 38·2, 37·4, 24·9, 20·6, 19·6sh
$Nb(S_2CN[CH_2]_4)_4$	1490	1170	1012	331	1·67; $\theta = 0$	40·2, 29·6, 22·4, 18·6
$Ta(S_2CN[CH_2]_4)_5$	1520	1162	1013, 980	335	Diamagnetic	38·4, 26·6

All the compounds are similar in colour to the *NN*-dialkyldithiocarbamates. The niobium derivative is purple rather than brown, as has been reported by other workers.[3] It appears that some decomposition occurs upon changing from purple to brown since the compound we prepared undergoes this colour change upon exposure to the atmosphere. The molybdenum and tungsten derivatives are fairly soluble in acetonitrile and only slightly soluble in 1,2-dichloroethane. The

---

[1] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152.

[2] J. N. Smith and T. M. Brown, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 441.

[3] D. J. Machin and J. F. Sullivan, *J. Less-Common Metals*, 1969, **19**, 413.

[4] D. C. Bradley and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 2741.

reverse solubility appears to be the case for niobium and tantalum. The tetramethylenedithiocarbamates are more air stable than the *NN*-diethyldithiocarbamates but tend to undergo slow hydrolysis and/or oxidation upon exposure to the atmosphere.

Infrared Spectra.—In recent years the i.r. spectra of numerous dithiocarbamate complexes have been reported.[1,5-7] In general these spectra are fairly complex. Fortunately, from a structural viewpoint it is only necessary to distinguish between unidentate and bidentate dithiocarbamate groups and a complete interpretation of the i.r. spectrum is not required. It is well known that most dithiocarbamate complexes contain chelated rings in which the ligand is co-ordinated to the metal through both sulphur atoms. From *X*-ray structural analysis Vaciago *et al.*[5,6] have determined that $Ru(NO)(S_2CNEt_2)_3$ contains one unidentate and two bidentate dithiocarbamate ligands while $Ru(S_2CNEt_2)_3$ contains three bidentate ligands. They found that the i.r. spectrum of the nitrosyl complex contained some absorptions which were absent in the tris-chelated complex. The presence of a band in the range 1460—1470 cm^{-1} in the $Ru(NO)(S_2CNEt_2)_3$ complex, which is close to the C–N stretch in sodium diethyldithiocarbamate, was advanced by these authors to be indicative of one unidentate ligand. However, in a later study by Bonati and Ugo,[7] it was shown that bands in the 1500 cm^{-1} region are not a very reliable indication of chelation. These workers made a thorough study of the i.r. spectra of some dithiocarbamate esters and dithiocarbamate complexes. They found that the absorptions in the 1500 cm^{-1} region were similar for both the esters and complexes, but the region *ca.* 1000 cm^{-1} displayed significant differences. If the dithiocarbamate ligand is bidentate, a single band *ca.* 1000 cm^{-1} is found which is due to two equivalent C–S stretching vibrations. In the case of unidentate dithiocarbamates, as in EtS_2CNEt_2, a doublet occurs at *ca.* 1005 and 983 cm^{-1} which is due to two non-equivalent C–S stretching vibrations. The authors conclude that this is a reliable criterion for determining the bonding mode of the dithiocarbamate ligand. This is also supported by the presence of a band *ca.* 980 cm^{-1} in $RuNO(S_2CNEt_2)_3$ which is absent in $Ru(S_2CNEt_2)_3$.

Inspection of the data in the Table shows that the niobium(IV), tungsten(IV), and molybdenum(IV) complexes contain only one medium absorption band *ca.* 1000 cm^{-1}. This would be indicative of these complexes being eight-co-ordinate with four bidentate dithiocarbamate ligands. Absence of an absorption band or shoulder in the 980 cm^{-1} region also suggests that the dithiocarbamate ligands are chelating in all cases. An absorption band is present *ca.* 1015 cm^{-1} in the spectrum of the tantalum(V) complexes which is due to a bidentate ligand. However, a band appears in the 980 cm^{-1} region which would indicate the presence of one or more unidentate ligands. While a co-ordination number of ten for the tantalum(V) complexes is possible, the band *ca.* 980 cm^{-1} supports a co-ordination number less than ten.

Bradley and Gitlitz[1] have reported far-i.r. data for some of the *NN*-dialkyldithiocarbamates. All these complexes had a strong band in the region 365—345 cm^{-1} which they assigned to the M–S stretching frequency. The bands in the 346—331 cm^{-1} region are assigned to the M–S stretching frequency in the tetramethylenedithiocarbamates.

Magnetic Data and Electronic Absorption Spectra.—The magnetic moments and electronic absorption spectra for the tetramethylenedithiocarbamates are listed in the Table. The magnetic moment for the niobium derivative approaches the spin only value of 1·72 B.M. and agrees well with that found for other eight-co-ordinate niobium(IV) complexes.[8-11] The *NN*-diethyldithiocarbamate derivative of niobium(IV) has been reported[1,3] to have a moment of *ca.* 0·5 B.M. However, this is much lower than the value of 1·57 B.M. we have obtained.[2] From the description of the compound, it appears that some decomposition may have taken place in those samples reported to have low moments. The molybdenum and tungsten derivatives have moments much smaller than the spin-only value of 2·83 B.M. but this is reasonable in view of the large spin–orbit coupling constants observed for these elements.

The electronic spectra of numerous dithiocarbamate derivatives have been reported in the literature. These complexes all exhibit two or three intense bands in the high energy region of the spectrum. The highest energy band occurs at 39 ± 3 kK and may contain a shoulder at *ca.* 35 kK.[12] Exact assignments of these bands have not been made, but it seems to be agreed that they are intraligand $\pi \longrightarrow \pi^*$ transitions located mainly in the CS_2 group.[13,14] A less intense band *ca.* 25—30 kK is either an $n \longrightarrow \pi^*$ intraligand transition[13] or a ligand-to-metal charge transfer.[14] In the tetramethylenedithiocarbamate derivatives intraligand transitions are noted above *ca.* 25 kK. The bands at lower energies are much less intense and are *d–d* transitions. These transitions are not obscured by charge transfer transitions as is often the case with nitrogen donor complexes. This data will be discussed in more detail in a

---

[5] M. Bonamico, G. Dessy, G. Mazzone, A. Mugnoli, A. Vaciago, and L. Zambornelli, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1963, **25**, 338.

[6] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476.

[7] R. Bonati and R. Ugo, *J. Organometallic Chem.*, 1967, **10**, 257.

[8] R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2865.

[9] J. B. Hamilton and R. E. McCarley, *Inorg. Chem.*, 1970, **9**, 1339.

[10] R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, 1970, **9**, 2305.

[11] J. N. Smith and T. M. Brown, *Inorg. Chem.*, 1972, **11**, in the press.

[12] G. St. Nikolov, N. Jordanov, and I. Havezov, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1059.

[13] M. J. Janssen, *Rec. Trav. chim.*, 1960, **79**, 151.

[14] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, A, **280**, 235.

later publication after more information becomes available.

EXPERIMENTAL

All the metal halides and most of the complexes prepared in this study were susceptible to both hydrolysis and/or air oxidation; therefore, all manipulations and reactions were carried out in a nitrogen atmosphere dry box or on a vacuum line. The metal halides were obtained either from commercial sources or prepared using accepted published methods. Ammonium tetramethylenedithiocarbamate was purified by recrystallization from ethanol. All solvents were thoroughly outgassed and dried prior to use.

Preparation of Metal Tetramethylenedithiocarbamates.—The appropriate metal chloride (*ca.* 0·005 mol) and a stoicheiometric amount of ammonium tetramethylenedithiocarbamate were placed in a reaction vessel.[15] Acetonitrile (*ca.* 50 ml) was added and the reaction mixture stirred for 24 h. The solution was filtered to remove the insoluble ammonium chloride. The acetonitrile was distilled off *in vacuo* and the desired product dried at 35 °C for 72 h under a dynamic vacuum. In the case of niobium and tantalum, the complexes were extracted with 1,2-dichloroethane after removal of acetonitrile from the reaction mixture.

Analytical Results.—Carbon, hydrogen, nitrogen, and sulphur analyses were determined by Alfred Bernhardt, Mulheim. The analytical data are given in the Table.

I.r. Spectra.—The i.r. spectra of all compounds were measured from 4000 to 200 cm^{-1} using a Beckman IR 12 grating spectrometer. Nujol mulls were prepared and sodium chloride plates were used for the 4000—600 cm^{-1} region. Polyethylene plates were used for the 600—200 cm^{-1} region. In addition to the bands listed in the Table, the compounds generally had bands in the following regions: 1333—1300m, 1251—1244m, 1220—1217m, 1110—1104m, 1039—1036m, 1013—1009m, 915—909w, 867—858w, 841—833m, 709—704w, 652—640w, 580w, 478—465s, cm^{-1}.

Electronic Absorption Spectra.—Spectra were recorded using a Cary model 14 recording spectrophotometer. Solutions in 1,2-dichloroethane were used in a 1 cm quartz cell constructed such that it could be closed off from the atmosphere.

Magnetic Data.—Magnetic susceptibility measurements were made *in vacuo* between liquid nitrogen and room temperature using the Faraday technique. Calibration was made using HgCo(SCN)_4 and all measurements were corrected for diamagnetism. The magnetic moments were obtained from the slope of plots of the corrected molar susceptibility *vs.* reciprocal temperature. Correction for the deviation from the Curie law was made where necessary.

[2/317 *Received*, 14*th February*, 1972]

---

[15] T. M. Brown and B. L. Bush, *J. Less-Common Metals*, 1971, **25**, 397.