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Metal Complexes of Di- and Mono-thiocarbamates and Related Compounds. I. Preparation and Characterization of Thallium(I) Compounds

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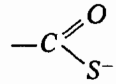
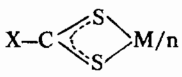
Thallium(I) monothiocarbamates and monothioxanthates have been prepared and characterized. The corresponding dithiocarbamato- and xanthato-Thallium(I) analogues have also been prepared and their properties compared.

Mass spectral, infrared spectral, pmr, and molecular weight measurements have been used to characterize the compounds.

The observation of strong bands in the infrared spectra of the monothiocarbamato- and monothioxanthato- compounds at 1525-1582 cm^{-1} and 665-675 cm^{-1} which do not occur in the dithio analogues are characteristic of the  *grouping.*

Introduction

The ability of the dithiocarbamato- and xanthato-groups to form complexes of type *1* [R=alkyl, aryl; X=R_2N–(dithiocarbamates, RO–(xanthates)] with a large number of metal ions in various oxidation states ($n \geqq 1$) is well established. The continuing interest in such species is indicated by the publication of recent review articles dealing with the preparation,[2] reactions,[2] and structural properties[2,3,4,] of these compounds.



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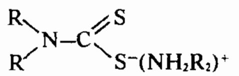
The dithiocarbamato- ligands are readily prepared by the reaction of carbon disulphide with a primary or secondary amine[5] to give the corresponding alkyl- or arylammonium salt of general form *2*. When the reaction is done in the presence of sodium or potassium hydroxides the corresponding alkali metal salts *3* are readily obtained.[6] Gleu and Schwab, using the sodium salts prepared from



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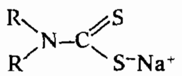

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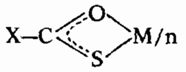
a variety of amines, indicated the versatility of these salts as ligands by showing that they reacted with over thirty different metal ions.[6]

The xanthato compounds are readily obtained by reaction of the appropriate metal alkoxide with carbon disulphide.[2]

Since there is current interest in the stereochemical consequences of oxygen *vs.* sulphur in the coordination sphere of metal complexes, particularly in bis-[4,7] and tris-chelate[8] metal complexes, we are presently investigating the *mono*-thio derivatives, *4*, where one of the sulphur donors in *1* has been replaced by oxygen. Future publications[9] will be concerned with transition metal complexes of this type.



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Parrod[10] has briefly examined the reaction of carbonyl sulphide with several secondary amines and has shown that alkylammonium salts of some monothiocarbamates can be readily prepared. These salts react with various metal ions[10] but the nature of the complexes so obtained has not been investigated. The purpose of our current investigations is to examine the general utility of carbonyl sulphide in the preparation of monothio- compounds and their metal complexes, *4*. The present paper deals with the preparation of some monothiocarbamato- and xanthato–Tl^{I} compounds and a comparison of their properties with the corresponding dithio analogues.

Akerstrom,[11] has prepared a series of dithiocarba-

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[1] On study-leave, 1970; Department of Chemistry, Trinity College, University of Dublin.

[2] D. Coucavanis, *Progr. Inorg. Chem.*, *11*, 233 (1970).

[3] R. Eisenberg, *ibid.*, *12*, 295 (1970).

[4] R.H. Holm and M.J. O'Connor, *ibid.*, *14*, 241 (1971).

[5] J. Von Braun, *Chem. Ber.*, *35*, 817 (1902).

[6] K. Gleu and R. Schwab, *Angew. Chem.*, *62*, 320 (1950).

[7] (a) D.H. Gerlach and R.H. Holm, *J. Amer. Chem. Soc.*, *91*, 3457 (1969); (b) D.H. Gerlach and R.H. Holm, *Inorg. Chem.*, *8*, 2292 (1969).

[8] (a) R.H. Holm, D.H. Gerlach, J.G. Gordon, II, and M.G. McNamee, *J. Amer. Chem. Soc.*, *90*, 4184, (1968); (b) J.G. Gordon, II, M.J. O'Connor and R.H. Holm, *Inorg. Chim. Acta*, *5*, 381 (1971).

[9] e.g. A series of bis(mono-thiocarbamato) Nickel(II) complexes of type *4* have been prepared and characterized (E. Krankovits, R.J. Magee, and M.J. O'Connor, *Inorg. Nucl. Chem. Lett.*, *7*, 541 (1971).

[10] J. Parrod, *Compt. Rend.*, *234*, 1062 (1952).

[11] S. Akersrom, *Arkiv Kemi*, *24*, 495 (1965).

mato–Tl^{I} compounds by the reaction of the alkali metal salts of the ligands with thallous sulphate and has shown that the compounds are dimeric in organic solvents.[12]

A recent x-ray structural determination[13] of the *n*–propyl derivative has shown it to consist of chains built from dimeric units in the solid state. Various xanthato–Tl^{I} compounds have been prepared[14,15] but they have not been studied in any detail. The corresponding monothio analogues of both types were not known.

Experimental Section

Preparation of Compounds. (a) *Reagents.* Potassium ethyl-xanthate and sodium diethyldithiocarbamate were commercial samples (British Drug Houses). Carbonyl sulphide was prepared by the action of dilute sulphuric acid on ammonium thiocyanate. Impurities (NH_3, HCN, CS_2) were removed by passage of the gas through a series of traps containing concentrated potassium hydroxide, concentrated sulphuric acid and finally a mixture of pyridine and nitrobenzene. In most experiments a cylinder of pure gas (Matheson Co. Inc.) was used. Thallous nitrate (B.D.H.) and thallous ethoxide (Emmanuel Ltd.) were used without further purification.

(b) *Ligands. Sodium pyrrolidinedithiocarbamate, Na(pyrroldtc)*, was prepared by the method of Gleu and Schwab.[6] A white crystalline material (dihydrate) was obtained, mp 295°. *Sodium pyrrolidinemonothiocarbamate, Na(pyrrolmtc).* Carbonyl sulphide was bubbled through pyrrolidine in the absence of solvent. The solution became warm and after several minutes a white precipitate formed. The precipitate was dissolved in 8 *M* potassium hydroxide and the solution thus obtained was allowed to cool to room temperature. Careful evaporation on a water bath gave a white compound which was washed with ethyl acetate and finally dried at 100°. The compound mp, 240-242°, is soluble in water and alcohol.

Anal. Calcd for $C_5H_{10}O_2NSK$ (monohydrate): C, 32.1; H, 5.4; N, 7.5; S, 17.1. Found: C, 32.8; H, 5.4; N, 7.5; S, 17.1.

(c) *Thallium(I) Compounds.* (1) *Thallium(I) diethyldithiocarbamate–Tl(Et₂dtc).* Thallous nitrate (0.27 g) in 75 ml water was added to 75 ml ethanol/water containing sodium diethyldithiocarbamate. The white precipitate obtained was allowed to stand for 2 hr and after filtration was washed with ethanol and dried at 105°. The compound is readily soluble in chloroform from which it was recrystallized, mp 114-115° (Lit.,[12] 116-118°).

Anal. Calcd for $C_5H_{10}NS_2Tl$: C, 17.0; H, 2.9; N, 4.0; S, 18.2. Found: C, 17.2; H, 3.0; N, 3.7; S, 18.2.

(2) *Thallium(I) diethylmonothiocarbamate–Tl(Et_2mtc).* The sodium salt of the ligand could not be isolated with a similar procedure to that used for the analogous dithiocarbamate. The thallium(I) compound was prepared *in situ* by the following method: Carbonyl sulphide was bubbled into diethylamine, ensuring that the temperature of the mixture was between 0 and 10°, until a white material diethylammoniumdiethylmonothiocarbamate formed. This product was dissolved in alcohol/water and an aqueous solution of thallous nitrate was added to give a cream coloured precipitate which coagulated after standing to give a buff-coloured material. The product was dried *in vacuo* to give the monohydrate. It appears to decompose between 40 and 50° and is extremely soluble in chloroform. However, attempts to recrystallize the product from chloroform or other organic solvents caused decomposition.

Anal. Calcd for $C_5H_{12}NO_2STl$: C, 16.9; H, 3.4; N, 4.0; S, 9.0. Found: C, 16.4; H, 3.0; N, 4.0; S, 8.9.

The compound decomposes gradually in the solid and after 24 hr gave the following analysis: C, 14.0; H, 2.4; N, 3.2.

(3) *Thallium(I) pyrrolidinedithiocarbamate–Tl(pyrroldtc).* Equimolar amounts of thallous nitrate and sodium pyrrolidinedithiocarbamate were reacted together in aqueous solution. The white precipitate which formed was allowed to stand for 2 hr, collected by filtration, washed with water and finally dried at 105°, mp, 150°. The compound does not decompose over long periods, and is only slightly soluble in organic solvents.

Anal. Calcd for $C_5H_8NS_2Tl$: C, 17.1; H, 2.3; N, 4.0; S, 18.3. Found: C, 17.1; H, 2.5; N, 3.8; S, 16.8.

(4) *Thallium(I) pyrrolidinemonothiocarbamate–Tl(pyrrolmtc).* This compound was prepared in an identical manner to the dithiocarbamate analogue using the potassium salt of the ligand. The compound isolated as the monohydrate, mp 115-116°, is off-white in colour. It is slightly soluble in organic solvents, and tends to decompose in the solid state after several days.

Anal. Calcd for $C_5H_{10}NO_2STl$: C, 17.0; H, 2.9; N, 4.0; S, 9.1. Found: C, 17.1; H, 2.6; N, 3.8; S, 8.9.

(5) *Thallium(I) ethylxanthate–Tl(Etxn).* Equimolar amounts of thallous nitrate and potassium ethylxanthate were reacted in water to give and off-white precipitate which was collected, washed throughly with water and finally dried at 105°. The product was recrystallized from chloroform to give an off-white product mp 130° (decomp.) (Lit,[14] 140°).

Anal. Calcd for $C_3H_5OS_2Tl$: C, 11.1; H, 1.6; S, 19.7. Found: C, 11.9; H, 1.6; S, 19.7.

(6) *Thallium(I) ethylmonothioxanthate–Tl(Etmtxn).* Carbonyl sulphide was bubbled into an ethanolic solution of Thallous ethoxide. A white precipitate formed and spread through the solution. The precipitate slowly changed to a copper-bronze colour

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[12] S. Akerstrom, *Acta Chem. Scand.*, *18*, 824 (1964).
[13] L. Nilson and R. Hesse, *ibid.*, *23*, 1951 (1969).
[14] J.R. Anderson, *Royal Aust. Chem. Inst. J. and Proc.*, *17*, 120 (1950).
[15] J.W. Spanyer and J.P. Phillips, *Anal. Chem.*, *23*, 253 (1956).

which indicates that it was decomposing slowly. The precipitate was collected and dried at 105°. It decomposes at approximately 120°, and attempts to recrystallize the compound caused decomposition.

Anal. Calcd for $C_3H_5O_2STl$: C, 11.6; H, 1.6; S, 10.4. Found: C, 12.5; H, 1.9; S, 8.5.

(c) *Physical Measurements.* Infrared spectra were obtained using mulls or discs on Perkin-Elmer 157 and 457 spectrometers. In the former, the range was 4000-650 cm^{-1}; in the latter 4000-250 cm^{-1}. Mass spectral data were obtained on a Hitachi Model RMS4 spectrometer. Pmr spectra were recorded on a Perkin-Elmer R10 Spectrometer using $CDCl_3$ solutions with tetramethylsilane as an internal reference. Molecular weights were measured on a Mechrolab Model 302A vapour phase osmometer calibrated with benzil.

(d) Analyses were performed by the Microanalytical Laboratory, University College, Dublin.

Results and Discussion

The thallium(I) monothio analogues of the dithiocarbamates and xanthates can be readily prepared in most cases by using carbonyl sulphide rather than carbon disulphide as the starting material. In general the monothio compounds, *4*, tend to decompose in both the solid state and in solution more readily than their dithio analogues, *1*.

Although the monothio derivatives are less soluble in organic solvents than the corresponding dithio compounds it has been possible in one case, that of Tl(Et$_2$mtc), to determine its molecular weight in chloroform at concentrations similar to those used by Akerstrom for Tl(Et$_2$dtc).[11] Both compounds are dimeric under these conditions. One important difference between these two compounds is that Tl(Et$_2$mtc) is isolated as a stable monohydrate (at least at temperatures <40-50°). The only structural data available for comparison is that for Tl(*n*—Pr$_2$dtc)[13] which has a structure consisting of chains built up from dimeric [Tl(*n*—Pr$_2$dtc)]$_2$ units with Tl - - - S coordination. The coordination sphere of the compound is best described as a distorted bipyramid in which the two thallium atoms occupy the apices. This compound has been shown to be dimeric in benzene.[11]

Mass spectral evidence for the existence of polymeric units in the present series of compounds was not definitive. The results and probable assignment of peaks are shown in Table I. The assignment of species containing Thallium and/or sulphur atoms is unambiguous because of the presence of ^{203}Tl, ^{205}Tl, ^{32}S, and ^{34}S isotopes.[16]

Four compounds, Tl(Etxn), Tl(Etmtxn), Tl(Et$_2$dtc), and Tl(Et$_2$mtc) were examined. In all cases the major m/e peaks were due to ^{203}Tl and ^{205}Tl isotopes. There is obviously a major break down of the molecular units of both Tl(Etxn) and Tl(Etmtxn) and peaks due to the monomeric parent ion were not detected. Strong peaks at m/e values corresponding to the monomeric molecular ion were observed for both Tl(Et$_2$dtc) and Tl(Et$_2$mtc). No trace of peaks due to polymeric species was detected. This observation may be due to the existence of only monomers for both of these compounds under the conditions necessary for observation of the mass spectra or polymeric (possibly dimeric) species which may exist in the solid phase break down in the spectrometer.

Table I. Mass Spectral Data for Thallium(I) Compounds.

Compound	m/e [a]
Tl(Etxn)	29(C_2H_5), 44(CS), 45(C_2H_5O), 60(OCS), 76(CS_2), 152(C_2S_4), 203(^{203}Tl), 205(^{205}Tl), 235(^{203}TlS), 237(^{205}TlS).
Tl(Etmtxn)	29(C_2H_5), 44(CS), 60(OCS), 73(C_2H_5OCO), 89(C_2H_5OCS), 203(^{203}Tl), 205(^{205}Tl).
Tl(Et$_2$dtc)	44(CS), 72($[C_2H_5]_2N$), 116($[C_2H_5]_2NCS$), 148($[C_2H_5]_2NCS_2$), 203(^{203}Tl), 205(^{205}Tl), 235(^{203}TlS), 237(^{205}TlS), 279($CS_2{}^{203}Tl$), 281($CS_2{}^{205}Tl$), 351($[C_2H_5]_2NCS_2{}^{203}Tl$), 353($[C_2H_5]_2NCS_2{}^{205}Tl$).
Tl(Et$_2$mtc)	44(CS), 60(OCS), 116($[C_2H_5]_2NCS$), 148($[C_2H_5]_2NCS_2$), 203(^{203}Tl), 205(^{205}Tl), 335($[C_2H_5]_2NCOS^{203}Tl$), 337($[C_2H_5]_2NCOS^{205}Tl$).

[a] Probable assignment of peaks in brackets.

Table II. Pmr spectra of Thallium(I) Compounds in $CDCl_3$ at ~30° [a].

Compound	shift, ppm [b]
Tl(Et$_2$dtc)	—3.97 (quartet, J=7Hz) —1.26 (triplet, J=6Hz)
Tl(Et$_2$mtc)	—3.50 (quartet, J=7Hz) —1.15 (triplet, J=8Hz)

[a] Shift at 60 MHz relative to tetramethylsilane as internal reference. [b] Centre of multiplet.

Pmr spectra of only Tl(Et$_2$dtc) and Tl(Et$_2$mtc) could be measured because of the lack of solubility of the other compounds in suitable solvents. The expected quartet (methylene protons) and triplet (methyl protons) occurring in the ratio 2:3 were found (Table II). No coupling of protons with thallium isotopes was detected.

The infrared spectra of dithiocarbamato- and xanthato-metal complexes have been extensively studied since Chatt and co-workers[17] established that a strong band which occurs between 1480 and 1542 cm^{-1} in a range of dithiocarbamato-compounds is due to a polar C=N double bond. More recent work[18] has shown that when hydrogen or aryl groups are attached to the nitrogen the band attributable to $\nu_{C=N}$ lies outside of this range. No such band occurs in the spectra of the xanthato-species. The resonance forms of the ligands can be expressed using valence bond formalism as shown in 5. Chatt *et al.*,[17] have concluded

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(16) W.L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1970, pp. 397-400.

(17) (a) J. Chatt, L.A. Duncanson, and L.M. Venanzi, *Nature, 177*, 1042 (1956); (b) J. Chatt, L.A. Duncanson, and L.M. Venanzi, *Suomen Kemi, B29*, 75 (1956).

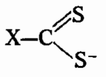
(18) (a) K. Nakamoto, J. Fujita, R.A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, 39, 423 (1963); (b) D. Coucavanis and J.P. Fackler, Jr., *Inorg. Chem.*, 6, 2047 (1967).

Table III. Infrared Spectral Data.

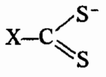
	Band position, cm$^{-1\,a,b}$
Tl(Etxn)	2970(s), 2940(w), 2922w(), 2876(w), 1480(w), 1454(m), 1438(w), 1412(w), 1378(m), 1345(w), 1262(w), 1165(s), 1132(w), 1110(sh), 1096(s), 1034(s), 1019(m), 1002(w), 446(s), 298(s).
Tl(Etmtxn)	2960(s), 2932(w), 2910(w), 2890(w), 1582(s), 1471(sh), 1464(m), 1440(m), 1376(m), 1348(m), 1160(sh), 1110(w), 1090(s), 1034(sh), 1019(w), 838(m), 808(w), 675(m), 505(m), 362(s).
Tl(Et$_2$dtc)	2959(s), 2919(m), 2880(sh), 2859(w), 1480(s), 1452(m), 1432(w), 1410(s), 1370(m), 1350(s), 1298(s), 1264(s), 1198(s), 1134(s), 1088(w), 1069(m), 978(s), 905(s), 835(s), 772(s), 565(s), 506(m), 470(w), 428(m), 392(m), 350(m), 330(m), 308(s).
Tl(Et$_2$mtc)	2959(s), 2919(m), 2882(sh), 2858(w), 1525(s), 1505(s), 1445(m), 1430(m), 1390(s), 1370(m), 1355(m), 1300(s), 1240(s), 1215(m), 1100(s),1060(sh) ,1004(w), 934(m), 862(s), 776(s), 665(s), 564(w), 488(m), 445(m), 384(m), 334(m), 326(m), 314(m), 301(m).
Tl(pyrroldtc)	2940(s), 2856(m), 1456(s), 1435(sh), 1430(sh), 1415(s), 1395(sh), 1370(sh), 1322(s), 1240(s), 1212(s), 1174(w), 1156(s), 1100(m), 1034(m), 988(s), 914(sh), 906(s), 855(m), 824(s), 695(s), 560(w), 446(s), 417(s), 348(w), 331(w), 320(w), 305(w), 295(s), 272(w), 260(w).
Tl(pyrrolmtc)	2942(m), 2848(m), 1538(s), 1508(sh), 1492(s), 1470(s), 1450(s), 1360(s), 1332(m), 1242(m), 1215(s), 1180(m), 1162(s), 1108(m), 1025(m), 968(m), 926(s), 903(s), 840(s), 736(s), 675(m), 662(w), 560(m), 480(s), 470(sh), 408(w), 360(s).

[a] Abbreviations in brackets refer to relative intensity of observed band: w, weak; m, moderate; s, strong; sh, shoulder.
[b] Measured as Nujol mulls and CsBr discs.

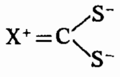
that *5c* makes a major contribution in the dithiocarbamates but is not important in the xanthates. However, recent studies[19,20] have indicated that a contribution from *5c* cannot be ignored completely in xanthato-complexes.



5a



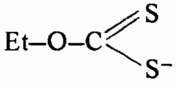
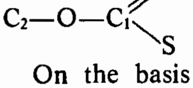
5b



5c

The main purpose of the present investigation is to assign the bands due to $\nu_{C=O}$ in the monothio- derivatives and to examine the infrared spectra of all of the thallium(I) compounds prepared. The only previous investigation of a thallium(I) species of this type is that briefly reported by Chatt[17b] for Tl(Et$_2$dtc) in the range 700-1300 cm^{-1}.

Tl(Etxn). The spectrum of this compound in the region 4000-250 cm^{-1} is divided into four groups of bands. The first group (2876-2970 cm^{-1}) is clearly due to C–H stretching frequencies and the second group in the range 1345-1480 cm^{-1} is assigned to CH$_3$ deformations.[19]

The third group which consists of bands in the region 1165-1002 cm^{-1} contains the major bands of the spectrum. A normal coordinate analysis on Ni(Etxn)$_2$ shows that all bands in the  $Et{-}O{-}C\genfrac{}{}{0pt}{}{\mathbin{/\!\!/}S}{\diagdown S^-}$ group are highly coupled.[20] Four bands occur at 1268, 1115, 1025, and 565 cm^{-1} which are due mainly to $\nu_{(C_1-O)}$, $\nu_{(C_2-O)}$, $\nu_{(C_1=S)}$, and $\nu_{(C_1-S)}$ of the  $C_2{-}O{-}C_1\genfrac{}{}{0pt}{}{\mathbin{/\!\!/}S}{\diagdown S}$ system respectively.

On the basis of the coordinate analysis and comparison of a range of compounds it has been concluded[20] that four characteristic bands occur in xanthates around 1200, 1100, 1025, and 565 cm^{-1}. Strong bands in Tl(Etxn) occur at 1165 cm^{-1}, 1096 cm^{-1}, and 1034 cm^{-1}. Despite many repetitions no band near 565 cm^{-1} has been observed in the present work. However, examination of published spectra of xanthate complexes[19] shows that this band is extremely weak when observed.

The final group of bands in Tl(Etxn) consists of two intense absorptions at 446 and 298 cm^{-1}. The 446 cm^{-1} band is assigned as mainly due to $\nu_{(Tl-S)}$ with some contribution from $\delta C_1{-}O{-}C_2$ by analogy with the results for Ni(Etxn)$_2$.[20] Ojima *et al.*,[21] have recently shown that metal-sulphur vibrations occur in this region and the intense band observed at 298 cm^{-1} in Tl(Etxn) is tentatively assigned to $\nu_{(Tl-S)}$.

Tl(Etmtxn). The infrared spectrum is similar to that of Tl(Etxn) although there are some significant differences. The most important difference is the occurrence of a strong band at 1582 cm^{-1} and a moderate band at 675 cm^{-1} in Tl(Etmtxn). The infrared spectra of a series of potassium salts of monothioxanthates reveal a very strong broad band at approximately 1580 cm^{-1} and a further sharp band at about 695 cm^{-1}. The former was assigned as $\nu_{C=O}$ and the latter to ν_{C-S}.[22] The close similarity of these bands in Tl(Etmtxn) and the fact that such bands are absent from the spectrum of Tl(Etxn) give strong support to similar assignments in the present compound.

Tl(Et$_2$dtc) and Tl(pyrroldtc). In both Tl(Et$_2$dtc) and Tl(pyrroldtc) strong bands occur at 1480 cm^{-1} and 1456 cm^{-1} respectively. These are due to the existence of the polar C=N partial double bond in *5c*. Strong to very strong bands occur in the region *ca.* 1450-700 cm^{-1}. The results of two normal co-

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(19) G.W. Watt and B.J. McCormick, *Spectrochim. Acta*, *21*, 753 (1965).

(20) U. Agarwala, Lashmi, and P.B. Rao, *Inorg. Chim. Acta*, *2*, 337 (1968).

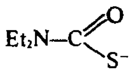
(21) I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto, and K. Tamura, *Inorg. Nucl. Chem. Lett.*, *6*, 65 (1970).

(22) F.G. Pearson and R.B. Stasiak, *Appl. Spectroscopy*, *12*, 116 (1958).

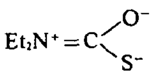
(23) G. Durgaprasad, D.N. Sathyanarayana, and C.C. Patel, *Can. J. Chem.*, *47*, 631 (1969).

ordinate analyses on metal dithiocarbamates[18a,23] have indicated that bands in the region 1350-1452 cm^{-1} can be attributed to degenerate symmetric and rocking vibrations of methyl groups. The strong absorption bands in the remainder of this region cannot be assigned because when the N–C=S group is present vibrational coupling effects will not allow assignment of C=S and C–S stretches. A band at 410 cm^{-1} in Ni(Me$_2$dtc)$_2$ has been assigned to a pure Ni–S stretching vibration with bands at 285, 385, 438, and 570 cm^{-1} having some contribution from a Ni–S stretchin mode.[23] Nakamoto *et al.*,[18a] have concluded that a band at *ca.* 357 cm^{-1} in M(Me$_2$dtc)$_2$ compounds is due to a M–S stretching vibration. Ojima *et al.*,[21] have concluded that three strong bands, whose frequencies are dependent on the central metal in a series of dithiocarbamates, are due to M–S stretching modes. The strong bands observed in Tl(Et$_2$dtc) and Tl(pyrroldtc) at 308 and 296 cm^{-1} respectively are probably due to $\nu_{(Tl-S)}$.

Tl(Et$_2$mtc) and Tl(pyrrolmtc). The presence of the C=O group in both compounds is shown by the appearance of bands which are absent in the corresponding dithio analogues. These moderate to strong bands occur at 1525 and 665 cm^{-1} for Tl(Et$_2$mtc) and 1538 and 675 cm^{-1} for Tl(pyrrolmtc). This behaviour is identical to that observed for Tl(Etmtxn), *vide supra.* Although a structure of type *6a* is important in these species a contribution from *6b* must also be considered since strong bands for Tl(Et$_2$mtc) and Tl-(pyrrolmtc) at 1505 and 1495 cm^{-1} respectively can reasonably be assigned to the polar C=N group.



6a



6b