*Contribution from the Department of Inorganic and Analytical Chemistry,
La Trobe University, Bundoora, Victoria 3083, Australia*

Monothiocarbamate Complexes of Rhodium(I)

E.M. Krankovits, R.J. Magee, and M.J. O'Connor

Received March 12, 1973

The preparation of some dicarbonyl(N-substituted-monothiocarbamato)rhodium(I) complexes is described. The red crystalline compounds are dimeric in chloroform solution and their infrared spectra in the terminal carbonyl region consist of three *bands. These observations suggest that the structure of the compounds is similar to that of* $[Rh(CO)_2Cl]_2$ *with the sulphur atoms of the monothiocarbamate ligands bridging the two rhodium(I) ions in the dimer. The reaction of the dimeric species with excess ligand and triphenyl-phosphine is also described. The monothiocarbamate acts as a monodentate ligand bonded through the sulphur atom only, in the products formed in these reactions.*

Introduction

The continuing interest in the study of metal complexes containing monothiocarbamate ligands is shown by the number of recent reports concerning various metal ions complexed with a variaty of N-substituted monothiocarbamates. These reports have concerned thallium(I)[1], nickel(II)[2,3,4,5,6], palladium(II)[3], platinum (II)[3], zinc(II)[7,8], cadmium(II)[8], mercury(II)[8], silver(I)[9] and copper(I)[10] compounds.

It has been shown that the stereochemistry of the monothiocarbamate complexes is normally different to that of the corresponding dithio– species, and in several cases, very pronounced differences have been found. Structural studies of bis (N,N-disubstituted-dithiocarbamato)nickel(II) complexes have shown that the compounds are monomeric and have essentially square planar $Ni{-}S_4$ coordination[11,12]. In contrast, the corresponding monothiocarbamato species are polymeric and have effective octahedral coordination[2,3,4,5]. No detailed structural analysis of these compounds is presently available but preliminary studies indicate that bis(N,N-di-*n*-propylmonothiocarbamato)nickel(II) is a hexamer, which has a cyclic chain structure involving bridging sulphur atoms in addition to chelate rings containing sulphur and oxygen atoms[5]. We have recently reported[6], the occurrence of weak ferromagnetic interactions in a series of these monothiocarbamato-nickel(II) complexes. The corresponding square-planar dithiocarbamate complexes are diamagnetic.

The X-ray crystal structure of bis(piperidine)-bis-(N-piperidylmonothiocarbamato)zinc(II) has shown that the two monothiocarbamate ligands are bonded to zinc through the sulphur atoms only and the piperidine molecules occupy the other two tetrahedral sites[7]. The average C-O and C-N bond lengths are 1.22(2) and 1.36(2)Å, respectively. These values are comparable to those found in organic amides where a double bond is delocalized over the C-O and C-N bonds. Recent studies on bis(tertiary phosphine)-bis(N–substituted–monothiocarbamato)palladium(II) compounds have indicated that similar monodentate coordination of sulphur occurs and proton magnetic resonance studies of the dimethylphenylphosphine derivative have established that the phosphine molecules are *trans* in the square-planar structure[3].

The isolation of rhodium(I) complexes containing the dithiocarbamate ligand has been achieved[13]. Several compounds of the type dicarbonylbis(N,N-di-R-substituted-dithiocarbamato)rhodium(I) (R = CH_3, C_2H_5), which are monomeric in solution and appear to involve bidentate coordination of the dithiocarbamate ligand have been reported[13]. The present paper outlines the preparation of some rhodium(I) monothiocarbamates and structural assignments of these complexes are made using mainly the results of infrared analysis.

Experimental Section

(a) *Preparation of dicarbonyl(N-substituted-monothiocarbamato)rhodium(I) compounds:*

Hydrated rhodium(III) chloride (1 g) was dissolved in refluxing absolute ethanol (15 cm^3) and carbon monoxide was bubbled vigorously through the solution until it was pale-yellow in colour (2 hr.)[14].

The yellow solution was filtered and cooled to room temperature and excess carbonyl sulphide was

---

(1) R.J. Magee and M.J. O'Connor, *Inorg. Chim. Acta*, *5*, 554 (1971).
(2) E.M. Krankovits, R.J. Magee, and M.J. O'Connor, *Inorg. Nucl. Chem. Letters*, *7*, 541 (1971).
(3) E.M. Krankovits, R.J. Magee and M.J. O'Connor, *Aust. J. Chem.* *26*, 1645 (1973).
(4) J. Willemse, *Inorg. Nucl. Chem. Letters*, *8*, 45 (1972).
(5) B.J. McCormick and B.P. Stormer, *Inorg. Chem.*, *11*, 729 (1972).
(6) E.M. Krankovits, R.J. Magee, K.S. Murray and M.J. O'Connor, *Aust. J. Chem.*, *26*, 749 (1973).
(7) C.G. Pierpont, D.L. Greene, and B.J. McCormick, *Chem. Commun.*, 960 (1972).
(8) B.J. McCormick and D.L. Greene, *Inorg. Nucl. Chem. Letters*, *8*, 599 (1972).
(9) P. Jennische and R. Hesse, *Acta Chem. Scand.*, *25*, 423 (1971).
(10) R. Hesse and A. Aava, *ibid.*, *24*, 1355 (1970).
(11) R.H. Holm and M.J. O'Connor, *Progr. Inorg. Chem.*, *14*, 241 (1971).
(12) P.W.G. Newman and A.H. White, *J. Chem. Soc.*, (*Dalton*), 1460 (1972).
(13) F.A. Cotton and J.A. McCleverty, *Inorg. Chem.*, *3*, 1398 (1964).
(14) J. Chatt and B.L. Shaw, *J. Chem. Soc.* (*A*), 1437 (1966).

passed into the solution. The appropriate secondary amine (0.25 g) was added dropwise to the stirred solution. The red precipitate which separated out almost immediately was collected, washed with a small amount of cold ethanol and recrystallized from chloroform or acetone. Yields in excess of 90 per cent based on the amine were obtained.

Analyses: *dicarbonyl(N,N-diethylmonothiocarbamato)rhodium(I)* - *(Et$_2$mtc)Rh(CO)$_2$* - Calcd. for $C_7H_{10}NO_3SRh$: C, 28.9; H, 3.5; N, 4.8; S, 11.0. Found: C, 29.2; H, 3.4; N, 4.7; S, 10.2. *dicarbonyl(N-pyrrolidylmonothiocarbamato)rhodium(I)* - *(pyrrmtc)Rh(CO)$_2$* - Calcd. for $C_7H_8NO_3SRh$: C, 29.1; H, 2.8; N, 4.9; S, 11.1. Found: C, 30.4; H, 3.1; N, 4.5; S, 10.1. *dicarbonyl(N-piperidylmonothiocarbamato)rhodium(I)* - *(pipmtc)Rh(CO)$_2$* - Calcd. for $C_8H_{10}NO_3SRh$: C, 31.7; H, 3.3; N, 4.6; S, 10.6. Found: C, 32.1; H,3.5; N, 4.6; S, 10.7.

(b) *Preparation of pyrrolidinium[dicarbonylbis-(N-pyrrolidylmonothiocarbamato)rhodium(I)]* - *[pyrrH] [(pyrrmtc)$_2$Rh(CO)$_2$]*: When excess secondary amine is added to the reaction mixture in (a) above, the red precipitate dissolves completely to give a yellow solution. In the preparation of the pyrrolidine derivative a yellow crystalline precipitate formed slowly. This precipitate was collected, washed with ethanol and air-dried. The yellow material decomposes slowly when stored in a sealed vessel.

Analysis: Calcd. for $C_{16}H_{25}N_3O_4S_2Rh$: C, 39.1; H, 5.3; N, 8.6; S, 13.1. Found: C, 39.0; H, 5.7; N, 8.6; S, 13.0.

Other derivatives, e.g. diethyl- and piperidyl compounds were not isolated because of their high solubility and apparent ease of decomposition.

(c) *Preparation of (carbonyl)bis(triphenylphosphine) (N,N-diethylmonothiocarbamato)rhodium(I)* - *(TPP)$_2$ (Et$_2$mtc)Rh(CO)*: When the stoicheiometric amount of triphenylphosphine was added to the yellow solution obtained in (b) for the diethylamine reaction, a light yellow microcrystalline material was precipitated. The precipitate was collected, washed with cold ethanol and air-dried. *Analysis*: Calcd. for $C_{42}H_{40}NO_2SP_2Rh$: C, 64.0; H, 5.1; N, 1.8; P, 7.9; S, 4.1 Found: C, 64.1; H, 5.3; N, 1.6; P, 8.1; S, 4.3.

(d) *Measurements*: Magnetic moments were determined by the Gouy method. Molecular weight measurements were made at 37°C in chloroform solution using a Mechrolab 301A vapour phase osmometer calibrated with benzil.

Infrared spectra were measured over the range 4000 250 cm^{-1} using a P.E. 457 spectrometer equipped with scale expansion. Potassium bromide discs, Nujol mulls or chloroform solutions of the compounds were used.

Conductance measurements were made on a Philips PR9500/02 bridge. Microanalyses were done by the Australian Microanalytical Service.

Results and Discussion

When the yellow solution formed by the reaction of carbon monoxide with hydrated rhodium trichloride in ethanol[14] is reacted with carbonyl sulphide in the presence of a secondary amine, high yields of red microcrystalline products are obtained which have stoicheiometry corresponding to $Rh(CO)_2$(N,N-disubstituted-monothiocarbamate).

Table I. Molecular weight data for rhodium(I) (monothiocarbamato)carbonyl compounds.[a]

Compound	Concn (g/dm^3)	Molecular Weight Found	Molecular Weight Calculated[b]
(pyrrmtc)Rh(CO)$_2$	10.0	600	289
	20.0	615	
(pipmtc)Rh(CO)$_2$	10.6	550	303
	21.3	590	

[a] $CHCl_3$ solution at 37°C. [b] For monomer.

The red solids, which may be recrystallized from chloroform or acetone, are diamagnetic in the solid state and the results in Table I indicate that they are dimeric in chloroform solution. Solutions of the compounds in chloroform are non-conducting.

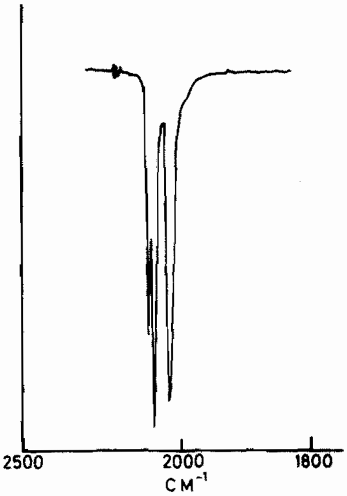

Figure 1. Infrared spectrum of [(pyrrmtc)Rh(CO)$_2$]$_2$ in chloroform.

The infrared spectra of the compounds in chloroform solution show three bands in the region characteristic of terminal C-O stretching modes[15]. The spectrum of [(pyrrmtc)Rh(CO$_2$]$_2$ in this region is shown in Figure 1. Similar spectra are found for [(Et$_2$mtc)Rh(CO$_2$]$_2$ and [(pipmtc)Rh(CO)$_2$]$_2$ and the absorptions for the three compounds are shown in Table II. The appearance of three bands in this region is similar to the behaviour of [Rh(CO)$_2$Cl]$_2$ which has been shown to consist of infinite chains of dimeric units each of which has two planes containing Rh(CO)$_2$Cl, bent at an angle of 124° along the line joining the two chlorines[16]. The infrared spectra of

---

(15) D.M. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold (Publishers) Ltd., London, 1967, p. 107.

(16) L.F. Dahl, C. Martell, and D.L. Wampler, *J. Am. Chem. Soc.*, 83, 1761 (1961).

(17) B.F.G. Johnson, J. Lewis, and P.W. Robinson, *J. Chem. Soc. (A)*, 2693 (1969).

Table II. Infrared spectra of rhodium(I)(monothiocarbamato)carbonyl compounds.

	Band position (cm^{-1}) [a]	
	ν_{C-O} [b]	$\nu_{C=O}$
[(Et$_2$mtc)Rh(CO)$_2$] [c]	2102(m), 2080(s), 2032(s)	1665(s), 1652(s) [d]
[(pyrrmtc)Rh(CO)$_2$]$_2$ [c]	2105(m), 2085(s), 2039(s)	1666(s) [d]
[(pipmtc)Rh(CO)$_2$]$_2$ [c]	2105(m), 2085(s), 2039(s)	1659(s) [d]
[pyrrH][(pyrrmtc)$_2$Rh(CO)$_2$] [d]	2055(s), 1975(s)	1567(s) [e,f]
(TPP)$_2$(Et$_2$mtc)Rh(CO) [d]	1987(s)	1557(s) [e]

[a] s = strong, m = medium intensity; [b] C–O stretch in metal-carbonyl; [c] chloroform solution; [d] KBr disk; [e] $\nu_{C=O}$, $\nu_{C=N}$ (see text); [f] δ_{N-H}, 1640 cm^{-1}.

the dimeric units in cyclohexane solution[17] for the species containing chloro, bromo, iodo, and mercapto bridging atoms are similar to those of the present compounds. The dimeric molecules containing the two planes at an angle have overall C_{2v} symmetry and the angled relationship should give rise to *one* symmetric and *two* antisymmetric ν_{C-O} absorptions, i.e. a total of *three* infrared active species. Such a pattern is observed for the monothiocarbamate complexes reported in this paper. Accordingly, the structure shown schematically in Figure 2 is suggested for these compounds, where the sulphur donor atoms are bridging the two rhodium(I) ions in the dimeric unit. This appears to be the first example of this type of bonding in monothiocarbamate complexes. Of further interest is the appearance of strong bands in the infrared spectra in the range 1652-1666 cm^{-1}. These absorptions are characteristic[18] of $\nu_{C=O}$ in systems of the type $-S-C(=O)NR_2$ and are appreciably shifted from $\nu_{C=O}$ observed in all other monothiocarbamate complexes so far reported which have only partial double bond character in both C–O and C–N bonds[3,5].

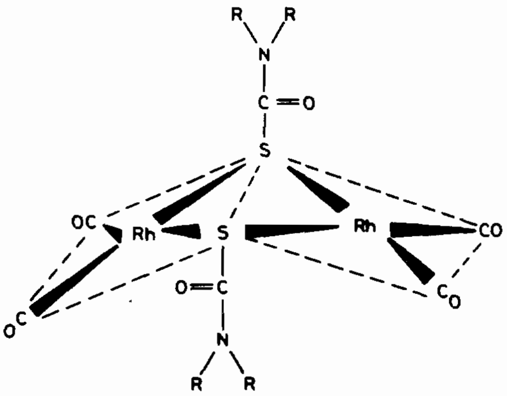

Figure 2. Suggested structure for dimeric dicarbonyl (N-substituted-monothiocarbamato)rhodium(I) compounds.

When excess amine is added to the reaction mixtures containing the red dimeric products, complete dissolution of the compound occurs and a yellow solution is obtained. When pyrrolidine was used a yellow crystalline product slowly crystallized from the solution. The infrared spectrum of the compound has an absorption at 1640 cm^{-1} which is due to δ_{N-H} arising from the pyrrolidinium ion.[5] Non-aqueous solutions of the compound are non-conducting but the parent pyrrolidinium-N-pyrrolidine-monothiocarbamate also behaves as a non-electrolyte under similar conditions. The infrared spectrum of the compound in the terminal carbonyl region[15] consists of a strong doublet (Table II) which indicates a *cis* arrangement of the carbonyl groups. The strong absorption at 1567 cm^{-1} may be assigned to $\nu_{C=O}$, $\nu_{C=N}$ since it is not normally possible to separate the two absorptions in these compounds[5]. The position of the absorption indicates monodentate coordination of the sulphur atoms. Similar bonding has been suggested for a series of square-planar palladium(II) monothiocarbamates[3]. The most likely structure of the anion in the present compound is square-planar with the 4-coordinate rhodium(I) ion bonded to two carbon monoxide molecules and two monodentate monothiocarbamate groups.

When excess diethylamine is added to the reaction mixture containing the red [(Et$_2$mtc)Rh(CO)$_2$]$_2$, a yellow solution results, and when triphenylphosphine is added, a pale yellow microcrystalline compound is obtained having a formula corresponding to (TPP)$_2$-(Et$_2$mtc)Rh(CO). Molecular weight measurements in chloroform, although not completely reliable because of the very low solubility of the compound indicate that the complex is monomeric. The infrared spectrum (Table II) has only one band (1987 cm^{-1}) which can be assigned as ν_{C-O} and the strong absorption at 1557 cm^{-1} indicates that the monothiocarbamate is probably bonded as a monodentate ligand through the sulphur atom. The triphenylphosphine groups are likely to be *trans* because this arrangement has been shown to occur in similar square-planar palladium(II) complexes containing monothiocarbamates[3].

---

(18) N.B. Colthup, L.H. Daly, and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964.