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Thiocarbamate Complexes.
IV. Synthetic Study Involving Iron, Molybdenum, Palladium and Platinum

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A comparative synthetic study of the ligational properties of thiocarbamate ($SOCNR_2$) *and dithiocarbamate* (S_2CNR_2) *monoanions has been carried out. The substitution of oxygen for sulfur along with the resulting decrease in chelate bite brings about a dramatic change in donor properties, as evidenced most clearly in the synthetic chemistry. In general, the synthetic chemistry of the thiocarbamate ligand is much more difficult and less predictable than is that for the dithiocarbamates. Specific new thiocarbamate compounds reported and characterized include:* $Fe(OSCNR_2)_3$, η^5-$C_5H_5Fe(CO)_2(OSCNC_4H_8)$, $Mo_2(OSCNC_4H_8)_4$, cis-$Pd(Ph_3P)_2(OSCNC_4H_8)_2 \cdot 2C_6H_6$, *and* cis-$Pt(Ph_3P)_2(OSCNC_4H_8)_2 \cdot 2C_6H_6$. *Also discussed are other iron and molybdenum systems for which dithiocarbamates are known to exist, but which do not provide analogous thiocarbamates. Finally, a new bonding mode for the thiocarbamate ligand is proposed.*

Introduction

Dithiocarbamate metal complexes have been known for many years, and studies involving all the transition metals have been reported. Coucouvanis [1] has reviewed the literature through about 1968. In contrast, interest in thiocarbamate complexes has developed only recently, the majority of the known complexes having been synthesized since 1970. At the present time complexes of the following metals have been reported: V(III) [2], Mn(I) [3, 4], Co(II) [5], Rh(I) [6, 7], Ni(II) [8], Pd(II) [9], Pt(II) [9], Cu(I) [10], Ag(I) [11, 12], Au(I) [7], Zn(II) [13], Cd(II) [13] and Hg(II) [13]. Sufficient work on the ligational properties of thiocarbamate ligands (abbreviated tic) is now available to permit one to draw several very general conclusions. First the syntheses of the thiocarbamate complexes are much more difficult and unpredictable than are those involving dithiocarbamates (abbreviated dtc). As a simple example, K_2PtCl_4 reacts readily in water with Nadtc to give $Pt(dtc)_2$ [14], whereas Natic gives no reaction [15]. A second generality is that the affinities of dtc and tic ligands for metal ions differ sharply. Thus, Co(II) reacts with dtc ligands to give Co(III)-dtc complexes along with the corresponding thiuramdisulfide [16, 17] whereas tic ligands give authentic Co(II) compounds [5]. Co(III) complexes of tic ligands have not been reported. Finally, it is clear that tic ligands give rise to a rich variety of bonding modes comparable to dtc ligands with the modes of coordination shown in Figure 1 now established unequivocally by X-ray techniques.

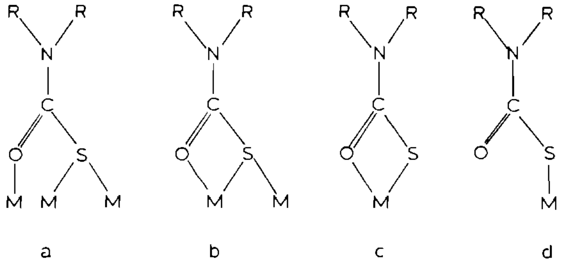

Figure 1. Coordination modes of tic ligands.

The present synthetic study was undertaken with the goal of further defining the ligational abilities of thiocarbamate ligands, especially as they contrast to those of the dithiocarbamates.

Experimental

Materials

Carbonyl sulfide (97.5%) was used as received from Matheson Gas Products. Amines were distilled from solid NaOH before use. Benzene was refluxed overnight using a Dean Stark trap to remove water. Tetrahydrofuran was distilled from CaH_2, and acetone was dried over $CaSO_4$ followed by distillation from P_4O_{10}. Anhydrous iron chloride was prepared by reacting iron wire with Cl_2 in acetonitrile [18]. The method of Johnson, Meyer and Winterton [19] was used to prepare $(\eta^5$-$C_5H_5)Fe(CO)_2Cl$. The starting materials *cis*-$(Ph_3P)_2PdCl_2$ and *cis*-$(Ph_3P)_2PtCl_2$ were prepared by the method of Jensen [20]. Molybdenum acetate was prepared from molybdenum hexacarbonyl, acetic acid, and N,N,N′,N′-tetramethylenediamine following the procedure of McCarley [21]. The method of Stiddard [22] was used to prepare $MoBr_2(CO)_3$bipy from $Mo(CO)_6$. Other solvents and chemicals were used as obtained from commercial sources.

Ligands

The sodium salt $Na(SOCNC_4H_8)$ was prepared as follows. A mixture of NaOH (4 g, 100 mmol) and pyrrolidine (9.0 ml, 7.65 g, 110 mmol) in 50 ml of anhydrous ethanol was stirred until the NaOH dissolved and the solution was filtered. Carbonyl sulfide was bubbled through this solution for 20 minutes, after which time the volume was reduced to 10 ml, and anhydrous ether was added. The white solid that formed was isolated by filtration and washed thoroughly with ether.

The cyclopentamethylene derivative, $Na(SOCNC_5H_{10})$, was prepared similarly.

The quaternary ammonium salts of thiocarbamate ligands, $(C_4H_8NH_2)(SOCNC_4H_8)$, $(C_5H_{10}NH_2)(SOCNC_5H_{10})$, and $(C_2H_6NH_2)(SOCNC_2H_6)$, were prepared as described in the literature [8]. The latter one was used in alcoholic solution and was not isolated.

Techniques

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls on CsBr plates or as chloroform solutions in NaCl solution cells. A Cary Model 14 recording spectrophotometer was used to obtain ultraviolet, visible, and near-infrared spectra. Mass spectra were obtained with a Nuclide 12-90-G single focusing mass spectrometer. Molecular weights were obtained with a Hitachi Perkin–Elmer Model 115 vapor phase osmometer. The instrument was calibrated with benzil in benzene. Magnetic moments were measured by the Gouy method. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Iron Compounds

$(\eta^5\text{-}C_5H_5)Fe(CO)_2(SOCNC_4H_8)$.

The ligand salt $Na(SOCNC_4H_8)$ (0.979 g, 6.4 mmol) was added to $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ (1.367 g, 6.4 mmol) in 75 ml of dry benzene. The resulting mixture was stirred and heated at reflux for 1 hour. The solution obtained was filtered and the filtrate was reduced in volume to 10 ml, after which pentane was added until precipitation began. Upon cooling the solution, red crystals formed, which were isolated by filtration and recrystallized from pentane. *Anal.* Calcd for $C_{12}H_{13}FeNO_3S$: C, 46.92; H, 4.27; N, 4.56. Found: C, 46.84; H, 4.14; N, 4.60%. Mol. Wt. Calcd: 307 g/mol. Found: 287 g/mol.

$Fe(SOCNC_5H_{10})_3$

All procedures were carried out under dry N_2 in a glove bag. Anhydrous $FeCl_3$ (1.201 g, 7.40 mmol) and $(C_5H_{10}NH_2)(SOCNC_5H_{10})$ (5.10 g, 22.2 mmol) were dissolved in dry, deaerated acetone (25 ml) and benzene (40 ml), respectively. The $FeCl_3$ solution was filtered into the ligand solution, and the resulting solution was stoppered and stored on ice for 20 minutes. The solution was then filtered. The deep red filtrate then was reduced in volume to 10 ml and filtered. The dark red, extremely air-sensitive precipitate that was collected was dried overnight *in vacuo* over P_4O_{10}. *Anal.* Calcd for $C_{18}H_{30}FeN_3O_3S_3$: C, 44.25; H, 6.20; N, 8.60. Found: C, 44.44; H, 6.30; N, 8.51%.

The compounds $Fe(SOCNC_2H_6)_3$ and $Fe(SOCNC_4H_8)_3$ were similarly prepared. *Anal.* Calcd for $C_9H_{18}FeN_3O_3S_3$: C, 29.35; H, 4.94; N, 11.41. Found: C, 29.66; H, 5.01; N, 11.37. Calcd for $C_{15}H_{24}FeN_3O_3S_3$: C, 39.98; H, 6.28; N, 9.33. Found: C, 39.73; H, 6.82; N, 9.24%.

Iron(II)

In a typical reaction an excess of $(C_4H_8NH_2)(SOCNC_4H_8)$ was added to a deaerated ethanolic solution of anhydrous iron(II) chloride under N_2. The brief appearance of a cream colored species was followed by the solution rapidly turning dark red or brown. No Fe(II) product was isolated.

Palladium and Platinum Compounds

cis-*$(Ph_3P)_2Pd(OSCNC_4H_8)_2 \cdot 2C_6H_6$*

The starting material, *cis*-$(Ph_3P)_2PdCl_2$, (1.00 g, 1.4 mmol) in 20 ml of THF was added to a slurry of $Na(SOCNC_4H_8)$ (0.428 g, 2.8 mmol) in 20 ml of THF. The slurry was stirred 3 hours and then filtered. The light green solid so isolated was dissolved in boiling benzene, filtered while hot to remove NaCl, and the solution cooled to yield a yellow product. *Anal.* Calcd for $C_{58}H_{58}N_2O_2P_2PdS_2$: C, 66.49; H, 5.59; N, 2.67. Found: C, 66.97; H, 5.49; N, 2.67%. Mol. Wt. (for non-solvated species): 892. Found: 854.

The corresponding platinum complex was prepared similarly from *cis*-$(Ph_3P)_2PtCl_2$ and $Na(SOCNC_4H_8)$. *Anal.* Calcd for $C_{58}H_{58}N_2O_2P_2PtS_2$: C, 61.30; H, 5.15; N, 2.46. Found: C, 61.91; H, 5.30; N, 2.50%.

Molybdenum Compounds

$Mo_2(SOCNC_4H_8)_4$

A freshly prepared sample of $Mo_2(O_2CCH_3)_4$ (0.305 g, 0.72 mmol) was suspended in deaerated, anhydrous ethanol in a Schlenk flask fitted with a fritted glass disk at the bottom. With dry N_2 passing through and over the solution, $Na(SOCNC_4H_8)$ (0.438 g, 2.86 mmol) in 10 ml of deaerated, anhydrous ethanol was added. A red precipitate formed immediately, and the mixture was stirred for 10 minutes until no remaining $Mo_2(OOCCH_3)_4$ could be seen. The ethanol then was removed by filtration and the solid remaining was washed with additional air-free ethanol. The reaction flask, now fitted with a flask containing P_4O_{10}, was evacuated. After drying the solid 3–4 hours, the reaction flask was transferred to a glove bag and the red solid was transferred quickly to vials under N_2. The product obtained in successful syntheses was bright red and extremely air sensitive (if at any time during the synthesis the product began to decompose, as evidenced by the product turning dark, the entire synthesis was abandoned; once decomposition started, the product could not be saved). *Anal.* Calcd for $C_{20}H_{32}Mo_2N_4O_4S_4$: C, 33.70; H, 4.53; N, 7.86; S, 17.99. Found: C, 33.82; H, 4.64; N, 7.71; S, 17.64%.

MoO_2Cl_2, Na_2MoO_4, $MoCl_4 \cdot 2py$, $Mo(CO)_6$, and $MoBr_2(CO)_3bipy$ with $(C_5H_{10}NH_2)(SOCNC_5H_{10})$ or $Na(SOCNC_4H_8)$

All the above molybdenum compounds were used as starting materials in attempted preparations of thiocarbamates. A variety of solvents and reaction conditions were used. In general, these were related to a known dithiocarbamate-metal complex preparation.

In this laboratory the presence of coupled ($C\underline{\cdots}N$, $C\underline{\cdots}O$) stretching frequencies around 1500–1600 cm^{-1} in the infrared region has been used successfully as a diagnostic tool in determining whether or not a thiocarbamate metal complex is present. In the present study it was concluded that no tic complex was formed if a strong and rather broad band in the 1500–1600 cm^{-1} region was absent in the reaction products, and it was assumed that the ligand decomposed under the reaction conditions used; however, no efforts were made to identify decomposition products.

MoO_2Cl_2

The compound MoO_2Cl_2 (2.049 g, 1.03 mmol) was added to a stirred solution of $(C_5H_{10}NH_2)(SOCNC_5H_{10})$ (4.738 g, 2.1 mmol) in deaerated acetonitrile under N_2. An orange precipitate formed after a few minutes. It was determined that the orange precipitate did not contain intact tic ligand.

Na_2MoO_4

The addition of thiocarbamate ligands to an aqueous solution of Na_2MoO_4 had various consequences depending on the pH of the solution. No change was noted in the solution upon addition of NaOH, while the addition of HCl caused gas evolution. Solids were isolated from the solutions by the evaporation of H_2O at reduced pressure. Infrared spectra of these solids exhibited no bands from 1500–1600 cm^{-1}.

$MoCl_4 \cdot 2py$

The compound $MoCl_4 \cdot 2py$ (0.50 g, 1.57 mmol) was added to an acetonitrile solution of $(C_5H_{10}NH_2)(SOCNC_5H_{10})$ (1.197 g, 5.25 mmol) and the mixture was stirred overnight. Upon removal of the acetonitrile at reduced pressure, an orange solid remained; however, intact thiocarbamate ligands were not present.

$Mo(bipy)(CO)_3Br_2$

A mixture of $MoBr_2(CO)_3bipy$ (0.853 g, 1.72 mmol) and $Na(SOCNC_4H_8)$ (0.492 g, 3.44 mmol) was stirred in deaerated CH_2Cl_2 under N_2 for 1 hour. The solution turned black during this time. Filtration yielded a white solid and a black solution that was evaporated to give an oil. Neither the solid nor the oil contained intact thiocarbamate ligand.

$Mo(CO)_6$

Refluxing a 2:1 mixture of $Na(SOCNC_4H_8)$ or $(C_4H_8NH_2)(SOCNC_4H_8)$ and $Mo(CO)_6$ in benzene for 12 hours gave a dark solution, which, after filtration and removal of benzene, afforded a brown oil that did not contain thiocarbamate ligands.

Results and Discussion

Iron Compounds

The addition of a thiocarbamate ligand to $FeCl_2$ leads to the formation of a transient cream colored species, which is believed to be an iron(II) thiocarbamate complex [23]. This compound was not isolated or characterized, and it seems unlikely that it will be studied in detail, except perhaps at low temperatures. In contrast, dithiocarbamate complexes of iron(II) can be synthesized, although they readily air-oxidize to the iron(III) derivatives [1, 16, 25].

Simple iron(III) complexes of dtc and tic ligands differ greatly [1]. The iron(III) dtc complexes are easily prepared and studied. On the other hand, the addition of a tic ligand to anhydrous $FeCl_3$ produces deep red, hydrolytically unstable $Fe(tic)_3$ [26] that is difficult to characterize because of its sensitivity to water and, probably, oxygen. When treated with water $Fe(tic)_3$ liberates OCS readily along with other unidentified hydrolysis products. Because of its instability little characterizational work was attempted on $Fe(tic)_3$. However, magnetic moments of the $Fe(OSCNC_5H_{10})_3$ and $Fe(OSCNC_2H_6)_3$ complexes were measured and found to be around 5.4 B.M., a value that is 0.3–0.6 B.M. lower than the experimentally expected moments of 5.7–6.0 B.M. found for most octahedral Fe(III) compounds [28]. Whether or not this reflects a spin equilibrium of the type observed in $Fe(dtc)_3$ complexes [1] was not ascertained [29]. The ($C\underline{\cdots}N$, $C\underline{\cdots}O$) stretching frequency, which is characteristic of tic compounds

[8], was found at 1535 cm^{-1} for $Fe(OSCNC_2H_6)_3$, 1520(br) cm^{-1} for $Fe(OSCNC_4H_8)_3$, and 1529 cm^{-1} for $Fe(SOCNC_5H_{10})_3$. These values are consistent with a formulation in which the ligand is bidentate.

In order to further probe the affinity of tic ligands for iron, the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ with thiocarbamates was investigated. Analogous dithiocarbamate systems have been studied, $(\eta^5\text{-}C_5H_5)Fe(CO)_2dtc$ and $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ having been isolated [30]. In the former case the dtc ligand is monodentate and in the latter it is bidentate. A corresponding thiocarbamate complex was prepared in this work from $Na(OSCNC_4H_8)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$. The compound is monomeric and soluble in common organic solvents such as acetone, $CHCl_3$, and benzene; it is stable indefinitely under ambient conditions. In principle the ligand can be bonded to the metal through either sulfur or oxygen. Studies [4, 9, 12, 31] to date have indicated that the sulfur atom is a better donor than oxygen, and since the compound is monomeric and retains two CO groups bonded to iron, we believe that the tic ligand in this complex is bonded to iron through the sulfur donor. The infrared spectral data strongly indicate this bonding mode as the $(C{\cdots}N, C{\cdots}O)$ frequency is quite high (1570 cm^{-1}), which suggests unbound oxygen in the tic ligand. A number of workers [7, 9, 15] have used the position of $\nu(C{\cdots}N, C{\cdots}O)$ to predict the bonding mode of the tic ligand. Values from 1503 cm^{-1} to 1545 cm^{-1} were taken to indicate a bidentate ligand and values above 1545 cm^{-1} were taken to indicate a monodentate sulfur-bonded tic ligand. Later work on tic complexes, including X-ray crystallographic studies [5], have contradicted this generalization. While the $(C{\cdots}N, C{\cdots}O)$ band position may be of some use in predicting the structure of tic complexes, the information cannot be regarded as unequivocal. If it can be determined that the ligand is monodentate, then sulfur, rather than oxygen, is the most likely donor, at least for the later transition metals. This would seem to be the case with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SOCNC_4H_8)$. X-ray studies relating to this point are currently in progress.

In contrast to the case of the dithiocarbamate complexes [32], neither heating the thiocarbamate compound for 24 hours in refluxing toluene nor irradiation of the compound in benzene with light from a Hg vapor lamp for 30 minutes lead to expulsion of a CO group with concomitant formation of a chelate ring. Under forcing conditions total decomposition of the complex occurred. These results are again evidence of the poor donor ability of the oxygen, which may be due in part to the small chelate bite of the tic ligand. The bite is approximately 0.3Å smaller than that of the dtc ligand.

Palladium and Platinum

Platinum and palladium readily form dtc complexes in the presence of tertiary phosphines; the compounds $(R_3P)M(S_2CNR_2)_2$ and $[Pt(S_2CNMe_2)(PR_3)_2]X$ where M = Pt, Pd; R_3P = tertiary phosphine; and X = S_2CNMe_2, $Cl{\cdot}H_2O$, PF_6 or BPh_4 were reported by Alison and Stephenson [33]. The reaction of *cis*-$(Ph_3P)_2PdCl_2$ or *cis*-$(Ph_3P)_2PtCl_2$ with $Na(SOCNC_4H_8)$ in THF leads to complexes of the type *cis*-$(Ph_3P)_2M(SOCNC_4H_8)_2$, M = Pt, Pd. The reactions proceed with the replacement of Cl^- and the tic ligand is believed to be monodentate. The compounds are monomeric, very slightly soluble in benzene and chlorobenzene and contain two molecules of benzene when recrystallized from C_6H_6. A base peak at 78 m/e in the mass spectra of the complexes confirms the presence of benzene. Samples from the original reaction (not recrystallized) contained no benzene. For *cis*-$(Ph_3P)_2Pd(SOCNC_4H_8)_2{\cdot}2C_6H_6$, $\nu(C{\cdots}N, C{\cdots}O)$ is at 1589 cm^{-1} while for the platinum derivative the corresponding band is at 1590 cm^{-1}. Coupled with the other information, the high values for this absorption suggest that the tic ligands are coordinated through the sulfur atom with the carbonyl oxygen atom remaining unbound to the metal.

Other tic complexes of palladium and platinum are reported in the literature, and in all cases, the tic ligand is considered to be bonded in a monodentate fashion through sulfur. Unfortunately, no X-ray crystallographic work has been carried out and all assignments are based mainly on infrared data. Krankovits, Magee, and O' Connor [9] have reported the formation of *trans*-$(Ph_3P)_2M(OSCNC_4H_8)_2$, M = Pt, Pd from OCS, K_2PtCl_4, triphenylphosphine, and amine, analogous to the *cis* isomers described above. The physical properties (*e.g.* solubilities) of the *trans*-complexes differ from those of the *cis*-complexes reported here, although the infrared spectra are essentially identical. This is reasonable and is consistent with the *cis vs. trans* formulation.

The use of *cis*-$(Ph_3P)_2MCl_2$, M = Pd, Pt, as a starting material for tic complexes could conceivably have led to a complex containing bidentate tic ligand. The fact that two tic ligands bond in a monodentate fashion again underscores the weak donor properties of the oxygen function. Further, with the large palladium and platinum metals the small ligand bite may be significant. The dtc ligand, which has a 0.3Å larger bite, is able to form bidentate complexes with those metals.

Molybdenum

The dithiocarbamate chemistry of molybdenum is extensive and syntheses of the complexes are straightforward in many cases. The compounds Na_2MoO_4 [34, 35], $MoCl_4$ [36], and $Mo(CO)_6$ [37] have been used as starting materials to prepare $MoO_2(dtc)_2$, $Mo(dtc)_3$ and $Mo(dtc)_4$, respectively. In contrast, we have been unsuccessful in preparing tic complexes starting with these compounds and using similar procedures. Again, poor oxygen donor ability, small

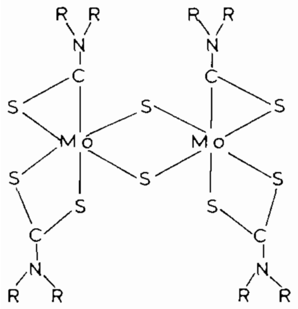

Figure 2. The molybdenum complex of dtc ligands.

ligand bite, or instability of products may prevent isolation of the desired products, or it may be possible that different reaction conditions could lead to molybdenum–tic complexes. In any case, the syntheses are not straightforward, and Mo–tic chemistry would appear to be much more complex synthetically than Mo–dtc chemistry.

In a quite novel reaction molybdenum acetate, $Mo_2(OOCCH_3)_4$, and $Na(S_2CNR_2)$ react to give the compound shown in Figure 2 [38]. The structure is confirmed by X-ray analysis [39].

The reaction of $Mo_2(OOCCH_3)_4$ with $Na(SOCNC_4H_8)$ gave a thiocarbamate complex of molybdenum which was bright red and extremely air sensitive. The compound analyzed empirically as $Mo(OSCNC_4H_8)_2$. As this analysis would be correct for a monomeric compound, a dimer with a structure similar to that above (Figure 2), or a dimer with a molybdenum acetate like structure, some effort was made to determine its structure. Mass spectral measurements were most useful, since the insolubility and high reactivity of the compound precluded most other measurements. Elemental molybdenum has seven naturally occurring isotopes which give seven lines over 9 m/e units in the spectra of monomers and 15 lines over 17 m/e units in the spectra of dimers [40]. The compound in question has several 15 line patterns over 17 m/e units, the most prominent appearing from 420–437 m/e. Therefore, we conclude that the compound is a dimer.

The frequency for ($C\underline{\cdots}N$, $C\underline{\cdots}O$) is quite low, being located at 1500 cm^{-1}. Despite the fact that infrared data may not be reliable as noted previously, this very low value almost certainly indicates the tic ligands in the complex are bridging.

The infrared spectrum in the region from 1220–600 cm^{-1} is essentially superimposable on the spectrum of $Zn(OSCNC_4H_8)_2$. [13]. This observation rules out a structure similar to that shown in Figure 2, since major changes would be expected in the infrared spectrum should the ligand lose either a sulfur or an oxygen atom. Thus, it is concluded that $Mo_2(SOCNC_4H_8)_4$ has a structure similar to that of molybdenum acetate. This conclusion also is supported by the observation that $Mo_2(SOCNC_4H_8)_4$ exhibits an electronic absorption band at 20,000 cm^{-1} (in acetone) in common with other compounds having the molybdenum acetate structure [41]. It should also be noted that it especially resembles a dimeric molybdenum–thiobenzoate complex prepared by Steele and Stephenson [36]. The two complexes have identical donor atoms and were prepared similarly. Although it can be concluded that $Mo_2(SOCNC_4H_8)_4$ has a molybdenum–molybdenum bond, the distribution of sulfur and oxygen atoms around the metals cannot be determined from the data in hand. The proposed structure for $Mo_2(tic)_4$ represents a new bonding mode for the tic ligand – one in which the ligand itself bridges two metals without additional sulfur bridging.

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References

1 D. Coucouvanis, *Prog. Inorg. Chem., 11,* 233 (1970).
2 A. M. Bond, A. T. Casey and J. R. Thackery, *Inorg. Chem., 13,* 84 (1974).
3 E. W. Abel and M. O. Dunster, *J. Chem. Soc. Dalton.,* 98 (1973).
4 K. Tanaka, Y. Muji-Uchi and T. Tanaka, *Inorg. Chem., 14,* 1545 (1975).
5 C. G. Pierpont, R. C. Dickinson and B. J. McCormick, *Inorg. Chem., 13,* 1674 (1974).
6 E. M. Krankovits, R. J. Magee and M. J. O'Connor, *Inorg. Chim. Acta, 7,* 528 (1973).
7 F. W. Pijpers, A. H. Dix and G. M. van der Linden, *Inorg. Chim. Acta, 11,* 41 (1974).
8 B. J. McCormick and B. P. Stormer, *Inorg. Chem., 11,* 729 (1972).
9 E. M. Krankovits, R. J. Magee and M. J. O'Connor, *Aust. J. Chem., 26,* 1645 (1973).
10 A. Fredga, *Rec. Trav. Chem., 69,* 416 (1950).
11 S. Akerstrom, *Acta Chem. Scand., 17,* 1187 (1963).
12 S. Araki, K. Matsumoto, K. Tanaka and T. Tanaka, *J. Inorg. Nucl. Chem., 38,* 727 (1976).
13 B. J. McCormick and D. L. Greene, *Inorg. Nucl. Chem. Letters, 8,* 599 (1972).
14 K. Nakamoto, J. Fujita, R. A. Condrate and Y. Morimoto, *J. Chem. Phys., 39,* 423 (1963).
15 B. J. McCormick, unpublished results.
16 J. P. Fackler, Jr. and D. G. Holah, *Inorg. Nucl. Chem. Letters, 2,* 251 (1966).
17 M. Delepine, *Bull. Chim. Soc. France, (4), 3,* 643 (1908).
18 B. J. Hathaway and D. G. Holah, *J. Chem. Soc.,* 2408 (1964).
19 E. C. Johnson, T. J. Meyer and N. Winterton, *Inorg. Chem., 10,* 1673 (1971).
20 K. A. Jenzen, *Z. Anorg. Chem., 229,* 225 (1936).
21 R. E. McCarley, Personal Communication.
22 M. H. B. Stiddard, *J. Chem. Soc.,* 4712 (1962).
23 After this paper was submitted for publication, a report on the synthesis and partial characterization of Fe(II)- and Fe(III)-thiocarbamates was published [24]. Although the synthetic procedures reported differ from ours, the

compounds appear to be identical.

24 H. Nakajima, T. Tanaka, H. Kobayashi and I. Tsujikawa, *Inorg. Nucl. Chem. Letters, 12,* 689 (1976).

25 K. Gleu and R. Schwab, *Angew. Chem., 62,* 320 (1950).

26 Another study [27] of Fe(III)-thiocarbamate complexes has very recently been brought to our attention. Again the synthetic procedures differ somewhat from ours, but the compounds prepared appear to be essentially the same.

27 L. J. Wilson, private communication.

28 A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, 1968, p. 34.

29 Nakajima, *et al.* reported [24] that the Fe(tic)$_3$ complexes are fully high-spin. On the other hand, Wilson [27] has found that the complexes exhibit spin-equilibrium characteristics, but that *fresh* samples must be used in order to observe these properties. It is clear that these compounds are exceptionally challenging to study because of their low stabilities. Our low magnetic moments may reflect sample decomposition.

30 C. O'Connor, J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A,* 84 (1969).

31 D. L. Greene, B. J. McCormick and C. G. Pierpont, *Inorg. Chem., 12,* 2148 (1973).

32 L. W. Houk and L. J. Epley, *Abstracts of Papers, ACS 165th National Meeting, Dallas, Texas,* 1973 (No. 80 Inorg.).

33 J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc. Dalton,* 254 (1973).

34 L. Malatesta, *Gazz. Chim. Ital., 69,* 408 (1939).

35 F. W. Moore and M. L. Larson, *Inorg. Chem., 6,* 998 (1967).

36 T. M. Brown and O. M. Smith, *J. Chem. Soc. Dalton,* 1614 (1972).

37 Z. B. Varadi and A. Nieuwpoort, *Inorg. Nucl. Chem. Letters, 10,* 801 (1974).

38 D. F. Steele and T. A. Stephenson, *Inorg. Nucl. Chem. Letters, 9,* 777 (1973).

39 L. Ricard, J. Estienne and R. Weiss, *Chem. Commun.,* 906 (1972).

40 E. Hochbert, P. Walks and E. H. Abbott, *Inorg. Chem., 13,* 1824 (1974).

41 J. G. Norman and H. J. Kolari, *J. Am. Chem. Soc., 97,* 33 (1976).