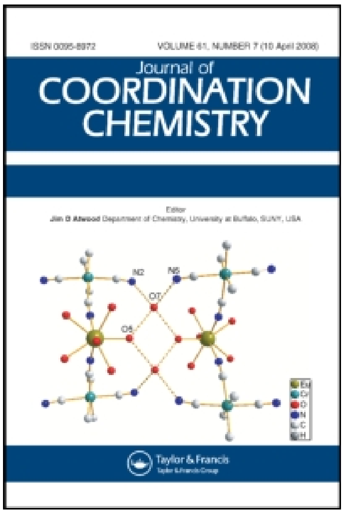

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Victoriano, Luis I. and Cortés, Hernán B.(1996) 'CUPROUS DITHIOCARBAMATES. SYNTHESES AND REACTIVITY', Journal of Coordination Chemistry, 39: 3, 231 — 239
To link to this Article: DOI: 10.1080/00958979608024331
URL: http://dx.doi.org/10.1080/00958979608024331

J. Coord. Chem., 1996, Vol. 39, pp. 231–239
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Printed in Malaysia

CUPROUS DITHIOCARBAMATES. SYNTHESES AND REACTIVITY

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(Received 4 December 1995; Revised 18 March 1996; In final form 11 April 1996)

Thiuram disulfides react with copper metal in organic solvents to afford copper(I) dithiocarbamates which are characterized by infrared, proton magnetic resonance and ESCA spectroscopies, as well as room temperature magnetic susceptibility measurements. These compounds react with some soft Lewis bases such as triphenylphosphine to give the bis-adducts, which are also isolated and characterized.

Keywords: cuprous; dithiocarbamates; thiuram disulfides

INTRODUCTION

Transition metal dithiocarbamates stand among the most studied compounds in inorganic chemistry and the subject has been critically reviewed.[1] This interest stems in part from the biological activity of the ligands, which results in extensive use as pharmaceuticals, fungicides, rubber vulcanization accelerators and quite recently in the therapy for HIV infections.[2] A more intradisciplinary aspect of dithiocarbamate chemistry is the recognized ability of the ligands to stabilize transition metals in unusually high oxidation states, a property which has been attributed to the ligand's ability to delocalize positive charge from the metal towards the periphery of the complex.[3] Univalent derivatives have been studied in only a handful of reports, which deal with silver(I), copper(I), gold(I) and thallium(I) compounds.[4]

Copper(II) dithiocarbamates are particularly well studied compounds due to their unique structural, magnetic and spectroscopic properties coupled to a relatively extensive electron transfer series. These are series of compounds

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(or ions) of the same composition and gross structure, differing only in the total number of electrons and thus in the actual charge of each of the members in the series.[3]

The chemistry of copper(I) dithiocarbamates, on the other hand, has remained largely unexplored. Synthetic procedures leading to these materials have included reaction of an alkali metal salt of the ligand with a cuprous compound, generally an oxide[5] or halide,[6] a procedure which yields products subject to halide contamination or oxidation to the cupric derivatives.[7] An alternative and more suitable approach is the reaction of thiuram disulfides with copper bronze suspended in an appropriate solvent.[8] This procedure has the advantage of affording highly crystalline material adequate for X-ray diffraction studies. A number of these studies have been completed. Unfortunately this information is not readily available.[9] Further characterization of copper(I) dithiocarbamates has included esr studies of the Et and i-Pr derivatives in solution as well as single crystal.[10]

As far as reactivity of copper(I) compounds is concerned, there have been studies dealing with halide oxidation which lead to either copper(III)[11] or copper(II) species. The latter are stabilized as a halocuprate(I) containing an oxidized form of the ligand system.[12] Other reports include syntheses of adducts with tertiary phosphines.[13] On the basis of solution molecular weight studies, ionic formulations involving ionic dtc$^-$ species (dtc$^-$ = NCS_2^-) have been proposed. This proposal has been reviewed and the results of the earlier studies have been attributed to partial dissociation of the phosphine ligands.[14]

Copper metal reacted with cupric dithiocarbamates or with thiuram disulfides, $R_2NC(S)S—SC(S)NR_2$ affords copper(I) dithiocarbamates in high yields. The coordination chemistry of these species has been explored using typical soft and hard ligands.

EXPERIMENTAL

General

The following materials were purchased from reliable suppliers: sodium dimethyldithiocarbamate dihydrate and tetraethylthiuram disulfide (Aldrich); sodium diethyldithiocarbamate trihydrate, triphenylphosphine, dimethylsulfoxide and copper powder (Merck); triphenylarsine and tetraethylethylenediamine (Eastman); and tetramethylthiuram monosulfide (Fluka). Bis—(N, N—dialkyldithiocarbamato) copper(II) compounds (alkyl=R=Me and Et) were prepared from stoichiometric amounts of the sodium salt of the corresponding dithiocarbamate and cupric sulfate pentahydrate (Merck) in hot aqueous solutions. The insoluble dark products were filtered hot, washed with 96% EtOH and air dried. Other tetraalkylthiuram disulfides[15] and monosulfides[16] were prepared as previously described. Instruments and analyses have also been described in previous publications. All compounds reported were diamagnetic at room temperature. Melting points were determined in a preheated apparatus.

ESCA spectra were run on a Fissons Instruments Escalab 220 iXL spectrometer with a monochromatic X-ray source. Charge compensation was achieved using a coaxial electron source. Spectra were calibrated using the C 1s line at Binding Energy (BE) 284.8 eV. Samples were mounted on double-sided adhesive tape. Other instruments have been described in previous publications.[15,16]

Preparation of copper(I) dithiocarbamates

Two general procedures were applied in the preparation of cuprous dithiocarbamates:

From tetraalkylthiuram disulfides

10 mmol of the corresponding disulfide was mixed with 30 to 40 mmol (large excess) of copper powder (electrolytic purity). 25 mL of carbon disulfide was added. The vessel holding the mixture was tightly capped and magnetically stirred for periods of time varying from 12 hours to 4 days. The dark color eventually discharged in the case of the Me and Et derivatives. For the i-Pr compound, a dark red-brown color remained after 4 days. The excess copper metal was removed by gravity filtration through filter paper and the solution was treated with hexane until turbid (Et) or a bright yellow solid had appeared (i-Pr). The solution containing the Et derivative was left in a freezer until needle shaped crystals were formed. When this procedure was applied to the i-Pr compound, some contamination of the yellow microcrystalline material with dark crystals was observed. The methyl derivative was obtained as an insoluble *café-au-lait* powder which could not be separated from the excess copper metal due to its lack of solubility in all solvents. The Et and i-Pr compounds were separated by filtration, washed with hexanes and air dried. Satisfactory elemental analyses were obtained without further purification.

From copper(II) dialkyldithiocarbamates

10 mmol of the corresponding dithiocarbamate (from sodium dithiocarbamate and copper sulfate, *vide supra*) was mixed with an equimolar amount (Me derivative) or threefold excess (Et derivative) of copper powder and carbon

disulfide (25 mL). The flask with the mixture was stirred magnetically until the dark color of the solutions had discharged (6 h for the Et, 3 days for the Me). The products were isolated as described in the previous paragraph. Preparation of the i-Pr compound was not attempted by this route.

(N,N-dimethyldithiocarbamato)copper(I), CuMe$_2$dtc: Café-au-lait amorphous powder, m.p. 270°(d). Yield: quantitative (method B). Anal. calcd. for $C_3H_6NS_2Cu$ (%): Cu, 34.58; C, 19.61; H, 3.30. Found: Cu, 34.46; C, 19.37; H, 3.14. IR(KBr): 2919w, 1500s, 1438sh, 1372s, 1242s, 1141m, 1047w, 963s, 556w. (Nujol): 441m, 327vw.

(N,N-diethyldithiocarbamato)copper(I), CuEt$_2$dtc (Procedure A): Pale yellow needles, m.p. 195–198°(d). Yield: 3.47 g (method B). Anal. calcd. for $C_5H_{10}NS_2Cu$ (%): Cu, 30.00; C,28.35; H, 4.77. Found: Cu, 30.17; C, 27.96; H, 4.56. IR(KBr): 2970m, 2927, 2864w, 1488s, 1452sh, 1415s, 1350m, 1263s, 1201s, 1142m, 1069m, 978m, 908m, 838m, 785w, 565w, 504w. (Nujol): 434w, 394w, 378vw, 325vw. ^{1}H-NMR($CDCl_3$): 4.00(q, 7.0 Hz, 2), 1.30(t, 7.0 Hz, 3).

(N,N-di-i-propyldithiocarbamato)copper(I), Cui-Pr$_2$dtc (Procedure A): Bright yellow microcrystalline solid, m.p 230°(d). Yield: 1.66 g. Anal. calcd. for $C_7H_{14}NS_2Cu$ (%): Cu, 26.49; C, 35.05; H, 5.89. Found: Cu, 26.18; C, 34.85; H, 5.76. IR(KBr): 2968m, 2926m, 2871w, 1478s, 1444s, 1379s, 1314vs, 1191s, 1141vs, 1035s, 929w, 850w, 771w, 585w. (Nujol): 479w, 320vw. ^{1}H-NMR ($CDCl_3$): 5.86(s,1), 3.96(s,1), 1.68(s,6), 1.23(s,6), all signals broad.

Preparation of triphenylphosphine complexes

A general procedure was employed for preparation of complexes of copper(I) dithiocarbamates and triphenylphosphine, which was as follows: 2.0 mmol of copper(I) dithiocarbamate was suspended in 25 mL of acetonitrile, 1.574 g (6 mmol) of PPh_3 was added and the mixture was stirred for three hours. A white amorphous solid was formed, which was filtered by suction and returned to the reaction vessel to be washed with two 10 mL portions of diethyl ether. The i-Pr derivative proved to be very soluble in ether and washing was carried out with a single 5 mL portion of cold (–15°) solvent. The products were filtered and air dried. All three products were chloroform soluble, white amorphous powders. Considering the tendency of R$_2$dtc—Cu(I)—PPh$_3$ compounds to rearrange in solution,[14] crystallization was not attempted.

Bis(triphenylphosphine)(N,N-dimethyldithiocarbamato)copper(I), Me$_2$dtcCu(PPh$_3$)$_2$: m.p. 193°. Yield: 1.40 g. Anal. calcd. for $C_{39}H_{36}NS_2PCu$ (%): Cu, 8.97; C, 66.13; H, 4.28. Found: Cu, 8.45; C, 65.95; H, 4.12. IR(KBr): 3049w, 2919w, 1950vs, 1890vw, 1820vw, 1480s, 1431s, 1371s, 1255m, 1134m, 1092m, 974m, 747s, 696 vs, 508s. (Nujol): 437w, 350w, ^{1}H-NMR ($CDCl_3$): 7.43–7.17(m,30), 3.31(s,6).

Bis(triphenylphosphine)(N,N-diethyldithiocarbamato)copper(I), *$Et_2dtcCu(PPh_3)_2$*: m.p. 147° Yield: 1.08 g. Anal. calcd. for $C_{41}H_{40}NS_2PCu$ (%): Cu, 8.63; C, 66.87; H, 5.49. Found: Cu, 8.32; C, 66.45; H, 5.55. IR(KBr): 3051w, 2974w, 2924w, 1950vw, 1890vw, 1820vw, 1478s, 1425s, 1267s, 1207w, 1129w, 1099m, 993w, 745s, 693vs, 512s. (Nujol): 439w. ^{1}H-NMR ($CDCl_3$): 7.45–7.10(m, 30), 3.88(q, 7.0, Hz, 4), 1.20(t, 7.0 Hz, 6).

Bis(triphenylphosphine)(N,N-diisopropyldithiocarbamato)copper(I), *$i\text{–}Pr_2dtcCu(PPh_3)_2$*: m.p. 174°. Yield: 1.16 g. Anal. calcd. for $C_{43}H_{44}NS_2PCu$ (%): Cu, 8.31; C, 67.55; H, 5.81. Found: Cu, 8.26; C, 67.33; H, 5.81. IR(KBr): 3050m, 1950vw, 1890vw, 1820vw, 1474s, 1434s, 1366m, 1305vs, 1196m, 1146m, 1091m, 1037m, 950w, 844w, 745s, 695vs, 509s. (Nujol): 432w, 327vw. ^{1}H-NMR ($CDCl_3$): 7.43–7.12(m,30), 5.68(s,1), 3.87(s,1), 1.40(s,12).

RESULTS AND DISCUSSION

Reaction of copper metal with thiuram disulfides has afforded copper(I) dithiocarbamates, which have been characterized by spectroscopy and reaction chemistry. The copper(I) dialkyldithiocarbamates prepared are diamagnetic, soluble solids and their solutions display conductivities typical of non electrolytes. These observations support the assignment of the structures as discrete molecular entities containing copper(I). An exception to this general trend is the dimethyl derivative, where lack of solubility prevented observation of conductivity and spectroscopic properties. In this case the solid state structure probably features a polymeric network of Cu....S bonded units extending in three dimensions.

The IR spectra of metal dithiocarbamates and related compounds have been thoroughly analyzed in the literature[17] and less comprehensively in previous articles of this series.[14–16] Three regions of the spectra are particularly informative with respect to the molecular structures of the compounds under study.

a) The region at *ca.* 1500 cm^{-1} features the thiureide band, which arises as a consequence of delocalization of the electron pair on nitrogen to the $R_2N—CS_2$ bond (polar canonical form). This effect increases the double bond character of the linkage and displaces the IR absorption from a value of 1250 cm^{-1} (typical of C—N stretch) to the value mentioned above. The position of this band is sensitive to electronic effects on the S atom and thus it is diagnostic of (formal) oxidation states on the coordinated metal center, among other factors.

This effect is apparent from inspection of the values in Table I. Differences of up to 30 cm^{-1} may be noted in going from Cu(I) to Cu(II) derivatives.

b) Electron donation from the S atom to the metal causes a shift of the C=S stretch from its typical position at 1200 cm^{-1},[18] to values close to 1000 cm^{-1}. This effect is also noted in the values given in Table I.

TABLE I Selected infrared frequencies for cuprous dithiocarbamates and their triphenylphosphine adducts

	$\nu_{C \doteq N}$	$\nu_{C=S}$	ν_{M-S}	$BE(eV)$
$Cu(I)Me_2dtc$	1500	963	327	932.5
$Cu(II)(Me_2dtc)_2$	1528	980	350	933.4
$Cu(Me_2dtc)(PPh_3)_2$	1480	974		932.6
$Cu(I)Et_2dtc$	1488	978	325	932.5
$Cu(II)(Et_2dtc)_2$	1508	998	355	
$Cu(Et_2dtc)(PPh_3)_2$	1478	993		932.5
$Cu(I)i{-}Pr_2dtc$	1478	1035	320	932.4
$Cu(i{-}Pr_2dtc)(PPh_3)_2$	1474	1037	327	932.5

All frequency values in cm^{-1}. See Experimental for corresponding band intensities.

c) M-S stretching frequencies for Cu-dithiocarbamate complexes appear in the region of 400 to 320 cm^{-1}, depending on the oxidation state of the metal. Very weak IR absorptions are seen in the spectra of all Cu(I)-dtc compounds reported in Table I. The position of these signals is consistent with their formulation as authentic Cu(I) dithiocarbamate compounds.

^1H-NMR data are presented for all compounds synthesized. Metal dithiocarbamates and allied thiuram sulfides display spectra consistent with restricted rotation about the $R_2N—CS_2$ bond, which causes magnetic nonequivalence of the R alkyl groups and splitting of the corresponding signals.[19] This effect is clearly observed in spectra of the isopropyldithiocarbamate-copper(I) compound. Two sets of methyne and methyl resonances are observed. The ethyl derivative must present a coalescence temperature below 23° (experimental probe temperature) since a typical pattern for a single ethyl group is observed. Pronounced broadening of the signals is apparent at lower temperatures (down to 5°).

Spectroscopic and analytical evidence indicate that bis(N,N-dialkyldithiocarbamato) copper (II) compounds are in all cases intermediates in the reaction of copper metal and thiuram disulfides,

$$R_2NC(S)—SC(S)NR_2 + Cu^\circ \longrightarrow Cu(S_2Nr_2)_2 \qquad (1)$$

oxidative insertion of the metal into the S—S bond of disulfides is precedented[20] and is ubiquitous reaction of thiuram disulfides. In fact, this constitutes a standard route to metal dithiocarbamates.[21] The reported reduction potential for thiuram disulfides (–0.34 V against the normal hydrogen electrode for the Me compound) makes these compounds very useful, mild oxidizing agents for metal species.[22]

Further reduction of the cupric derivative with excess copper metal is an alteration of the well known comproportionation equilibrium of copper(I), enhanced by the slight solubility of the cuprous species.

$$Cu(S_2CNR_2)_2 + Cu^\circ \longrightarrow 2CuS_2CNR_2 \qquad (2)$$

A natural extension of this sythesis and structural study of copper(I) diakyldithiocarbamates involves the preparation of adducts with selected soft and hard ligands. It is to be expected that the softish Cu(I) acid would have better affinity for soft phosphine and sulfide ligands instead of hard sulfoxide or amine counterparts.

This expectation was only partly realized in the present study. The chelating N,N,N′,N′-tetraethylethylenediamine failed to cause dissolution of a suspension of N,N-dimethyldithiocarbamatocopper(I) in acetonitrile at room temperature. Long reaction times caused darkening of the solution due to air oxidation of the cuprous species. Similar observations were made with dimethylsulfoxide. Surprisingly, the soft ligands triphenylarsine and tetramethylthiuram monosulfide also failed to react with copper(I) dithiocarbamates.

Addition of triphenylphosphine to suspensions (Me compound) or solutions (ethyl and isopropyl derivatives) of cuprous dithiocarbamates caused immediate signs of reaction and after suitable amounts of time, almost quantitative yields of the corresponding bis-adduct were isolated. These adducts are white, diamagnetic solids with analyses consistent with the proposed formulation and dissolve in chloroform to give non conducting solutions. Their spectroscopic properties, summarized in Table I (IR) and in the Experimental section for each compound (^{1}H-NMR), are consistent with our formulations. The low intensity bands at *ca.* 3050 cm^{-1} and between 1800 to 2000 cm^{-1} 10, are assigned respectively, as the stretch of an aromatic C—H bond and of a C═C in the phenyl ring,[18] both confirm the presence of PPh_3.'This is also supported by the appearance of the corresponding phenyl resonances close to 7 ppm in the proton magnetic resonance spectra. Slight displacements of the thiureide band to lower wavenumbers and of the C═S frequency to higher values are consistent with P sigma donation to Cu(I) and M—S diminished back donation. This causes more delocalization of an S electron pair over to the CuS_2 chelate ring. This enhanced electron density prevents contribution from the polar S_2C—NR_2 form to the total resonance hybrid and lowers the C—N frequency as shown from inspection of the values from Table I. A similar argument accounts for the increase in values observed for $\nu_{C=S}$. Interestingly these effects decrease in importance as one goes from the Me to Et and i-Pr compounds. Such a trend would seem to indicate that the lighter homologues form stronger adducts. No further evidence is available to support this speculation.

Further support for the assigned oxidation state in the series of compounds prepared is available from ESCA spectroscopy. Significant differences may be observed in the spectra of cupric compounds when compared to cuprous analogs. Thus the copper(I) state is characterized by values of 932.5 eV Binding Energy (BE),[23] while for the divalent state the values expected are about 1 eV higher, with intense shake-up satellites at 945–948 eV. All the samples synthesized show features attributable to the Cu(I) state. Furthermore, additional signals, consistent with the Cu(II) state, are apparent in all the Cudtc compounds within two to three days. These features remain absent in the spectra of the triphenylphosphine adducts, indicating enhanced stability to air oxidation.

Acknowledgments

Support was available from Universidad de Concepción (Dirección de Investigación PI 94-21-0.1-1) and from a joint fund by International Copper Association and Centro de Investigación Minera y Metalúrgica (ICA-CIMM).

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