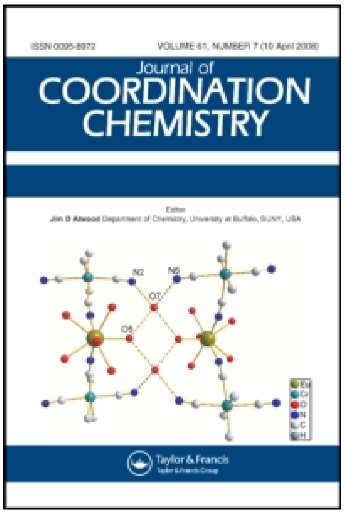

Journal of Coordination Chemistry

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

Reaction of Mixed Benzoicdithiocarbamic Anhydrides with Copper(II) Bromide

K. K. Mohammed Yusuff[a]; E. J. Mathew[a]
[a] Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, India

To cite this Article Yusuff, K. K. Mohammed and Mathew, E. J.(1992) 'Reaction of Mixed Benzoicdithiocarbamic Anhydrides with Copper(II) Bromide', Journal of Coordination Chemistry, 26: 2, 133 — 135

To link to this Article: DOI: 10.1080/00958979209407922

URL: http://dx.doi.org/10.1080/00958979209407922

J. Coord. Chem. 1992, Vol. 26. pp. 133-135
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

REACTION OF MIXED BENZOICDITHIOCARBAMIC ANHYDRIDES WITH COPPER(II) BROMIDE

K. K. MOHAMMED YUSUFF* and E. J. MATHEW

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India

(Received 9 September 1991; in final form 30 November 1991)

The reaction of mixed benzoicdithiocarbamic anhydrides with copper(II) bromide in diethylether leads to mixed oxidation state complexes of the type $[Cu_3(DTC)_6]^{2+}[Cu_2Br_6]^{2-}$, where DTC is a dithiocarbamate ligand. Conductance and magnetic measurements, infrared and electronic spectral data suggest that these complexes contain two $[Cu^{III}(DTC)_2]^+$ units and one $[Cu^{II}(DTC)_2]$ unit. They appear to be similar to $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ (Bu_2dtc=di-*n*-butyldithiocarbamate), the structure of which has already been established.

Keywords: Benzoicdithiocarbamic anhydrides; copper(II) bromide; mixed oxidation states; copper(II and III) dithiocarbamate complex

INTRODUCTION

A series of bis(dithiocarbamato)-μ-dichlorodicopper(II) complexes have been prepared by reacting mixed benzoicdithiocarbamic anhydride with copper(II) chloride in acetone.[1] While investigating this reaction with copper(II) bromide in diethylether, we were able to isolate complexes of the type $[Cu_3(DTC)_6]^{2+}[Cu_2Br_6]^{2-}$ (where DTC = diethyldithiocarbamate (Et_2dtc), pyrrolidine-*N*-carbodithioate (Pyrrdtc), piperidine-*N*-carbodithioate (Pipdtc), or morpholine-*N*-carbodithioate (Morphdtc)) in which copper atoms exist in +2 and +3 oxidation states.

EXPERIMENTAL

Mixed benzoicdithiocarbamic anhydrides were prepared according to procedures reported earlier.[2,3] The complexes were synthesized by the following general method: anhydrous $CuBr_2$ (1.1 g, 0.005 mol) and the appropriate freshly recrystallised benzoicdithiocarbamic anhydride (0.006 mol), both dissolved in minimum quantity of diethylether, were mixed with stirring, when a black complex separated out immediately. The complex was filtered off, washed with diethylether and dried *in vacuo* over P_2O_5.

Anal.: Calcd. for $[Cu_3(Et_2dtc)_6][Cu_2Br_6]$: C, 21.36; H, 3.56; N, 4.98; Cu, 18.84; Br, 28.45; S, 22.79%. Found: C, 21.26; H, 3.48; N, 4.92; Cu, 18.70; Br, 28.35; S, 22.75%. Calcd. for $[Cu_3(Pipdtc)_6][Cu_2Br_6]$: C, 24.58; H, 3.41; N, 4.78; Cu, 18.07; Br, 27.29; S, 21.85%. Found: C, 24.48; H, 3.35; N, 4.73; Cu, 18.00; Br, 27.19; S, 21.82%. Calcd.

---

*Author for correspondence.

for $[Cu_3(Pyrrdtc)_6][Cu_2Br_6]$: C, 21.52; H, 2.86; N, 5.02; Cu, 18.99; Br, 28.66; S, 22.95%. found: C, 21.44; H, 2.77; N, 4.98; Cu, 18.85; Br, 28.58; S, 22.92%. Calcd. for $[Cu_3(Morphdtc)_6][Cu_2Br_6]$: C, 20.35; H, 2.71; N, 4.75; Cu, 17.95; Br, 27.08; S, 21.73%. Found: C, 20.28; H, 2.69; N, 4.68; Cu, 17.85; Br, 27.01; S, 21.68%.

Analytical methods

Copper and sulfur analyses were carried out using standard procedures.[4] Microanalyses for C, H and N were performed on a Perkin Elmer 2400 CHN elemental analyser. Conductance measurements in nitrobenzene were carried out on a Elico PR 9500 conductivity bridge. Corrected molar susceptibilities (χ'_M) at room temperature (28 ± 2°C) were determined using the Guoy method.[5] Electronic and infrared spectra were recorded on a Hitachi U-3410 spectrophotometer and on a Perkin Elmer 983 spectrophotometer, respectively.

RESULTS AND DISCUSSION

All complexes are black in colour, quite stable in dry atmosphere, and insoluble in non-polar solvents like chloroform, diethylether and carbontetrachloride, but are moderately soluble in acetone, nitrobenzene, DMF and DMSO.

Analytical data suggest a general molecular formula $[Cu_3(DTC)_6]^{2+}[Cu_2Br_6]^{2-}$ for the complexes. Cras *et al.*[6] have earlier reported the structure of a similar complex, $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ (Bu_2dtc = di-*n*-butyldithiocarbamate), prepared by reacting $[Cu(Bu_2dtc)_2]$ with $CdBr_2$ and Br_2. The cationic part of this complex contains a copper(II) dithiocarbamate unit sandwiched between two copper(III) dithiocarbamate units with sulfur bridging between copper atoms.

The conductance values of the complexes (~60 ohm^{-1} cm^2 mol^{-1}) suggest a 2:1 electrolytic behaviour in nitrobenzene,[7] which may be due to the following dissociation reaction:

$$[Cu_3(DTC)_6]^{2+}[Cu_2Br_6]^{2-} \rightarrow 2[Cu(DTC)_2]^{+} + [Cu(DTC)_2] + [Cu_2Br_6]^{2-}$$

The μ_{eff} value of 1.9 BM for the $[Cu_3(DTC)_6]^{2+}$ species indicates that one of the copper atoms in it is in the +2 oxidation state and the other two are in the +3 oxidation state. This μ_{eff} value was calculated using the χ'_M value for $[Cu_3(DTC)_6]^{2+}$ obtained by subtracting the χ'_M value (660×10^{-6} cm^3 mol^{-1}) of $(IPA)_2[Cu_2Br_6]$ (IPA = isopropylammonium cation)[8] from that (~2200×10^{-6} cm^3 mol^{-1}) of $[Cu_3(DTC)_6]^{2+}[Cu_2Br_6]^{2-}$.

Further indication about mixed oxidation states has been obtained from the solid state electronic spectra of the complexes, which exhibit bands characteristic of copper(II) (~22500 cm^{-1})[9] and copper(III) (~26000 cm^{-1} and ~15500 cm^{-1})[10] dithiocarbamates. A band is also seen at 19000 cm^{-1} which may be due to the presence of $[Cu_2Br_6]^{2-}$, as a band at this frequency is observed in the spectrum of $(IPA)_2[Cu_2Br_6]$. Infrared spectra of the complexes also give evidence in support of mixed oxidation states: the spectra show ν(C–N) bands due to copper(II) dithiocarbamate[11] at ~1480 cm^{-1} and to the copper(III) dithiocarbamate[12] at ~1540 cm^{-1}. The intensity of the 1540 cm^{-1} band is almost twice that of the 1480 cm^{-1} band, which suggests that there are two copper(III) units and one copper(II) unit. The complexes also exhibit ν(Cu–S) bands due to copper(II)

($\sim 340\,\mathrm{cm}^{-1}$) and copper(III) ($\sim 400\,\mathrm{cm}^{-1}$) dithiocarbamates.[11] The observed higher intensity of the $400\,\mathrm{cm}^{-1}$ band tends additional support to the presence of two copper(III) dithiocarbamate units. All the above facts suggest that the complexes reported herein are structurally similar to the complexes prepared by Cras *et al.*[6]

REFERENCES

1. C.G.R. Nair and K.K.M. Yusuff, *J. Inorg. Nucl. Chem.*, **39**, 281 (1977).
2. D.S. Tarbell and R.P.F. Sharrer, *J. Org. Chem.*, **27**, 1972 (1962).
3. P.G. Nair and C.P. Joshua, *Tetrahedron Lett.*, **47**, 4785 (1972).
4. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longmans-Green, London, 1968).
5. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
6. J.A. Cras, J. Willemse, A.W. Gal and B.G.M.C. Hummelink-Peters, *Rec. Trav. Chim. Pays-Bas*, **92**, 641 (1973).
7. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. D.R. Bloomquist and R.D. Willett, *J. Am. Chem. Soc.*, **103**, 2615 (1981).
9. D. Coucouvanis, *Progress in Inorganic Chemistry*, **11**, 234 (1970).
10. P.T. Beurskens, J.A. Cras and J.J. Steggerda, *Inorg. Chem.*, **7**, 810 (1068).
11. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley Interscience, New York, 1968).
12. J. Willemse, J.A. Cras, J.J. Steggerda and C.P. Keijers, *Structure and bonding*, **28**, 83 (1976).