A Non-symmetric Di(benzenethiolato)cuprate(I) from the Demetallation of *N,N'*-Ethylenebis(acetylacetoniminato)copper(II)

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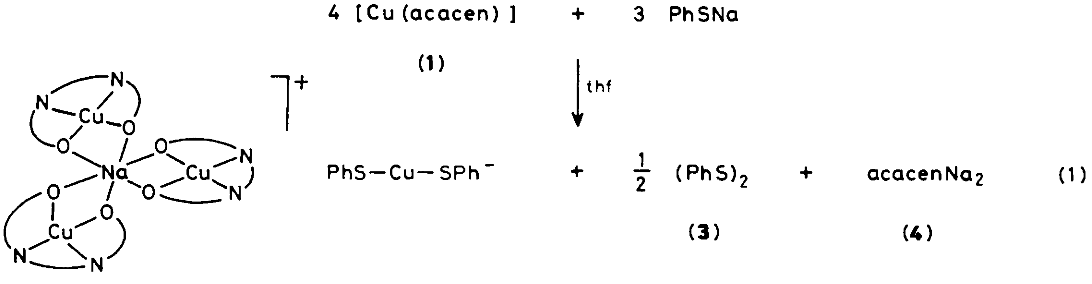
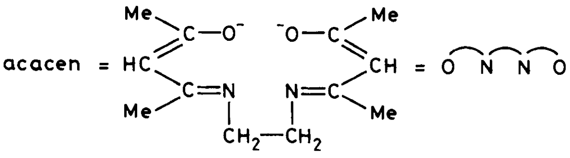
Demetallation of [Cu(acacen)] [acacen = *N,N'*-ethylenebis(acetylacetoniminato) dianion] by PhSNa produced the ion-separated dithiocuprate(I), $\{[Cu(acacen)]_3Na\}^+[Cu(SPh)_2]^-$ containing two forms of the PhS^- anion, as confirmed by a single crystal *X*-ray diffraction study.

Reaction of transition metal Schiff base complexes with alkali metal salts leads to polymetallic[1—3] or polyfunctional systems,[4] resulting from the complexation either of the naked alkali cation[2] or of its ion-pair with a co-ordinating anion.[3] In the latter case, depending on the nature of the transition metal, simultaneous co-ordination of the anion to the transition metal can occur.[5] Both results have been observed in the complexation of sodium ethoxide[5] and sodium benzenethiolate[6] with [M(acacen)] [M = Fe, Co, Ni; acacen = *N,N'*-ethylenebis(acetylacetoniminato) dianion].

The reaction of [Cu(acacen)] with PhSNa gave an unusual result which is significant in the context of copper–thiolate chemistry[7] and the complexation of alkali cations.[1—4] On treating a tetrahydrofuran (thf) solution of (**1**) with an equimolar amount of PhSNa dissolved in the same solvent, a microcrystalline violet solid formed. The solid was extracted



(**2**)



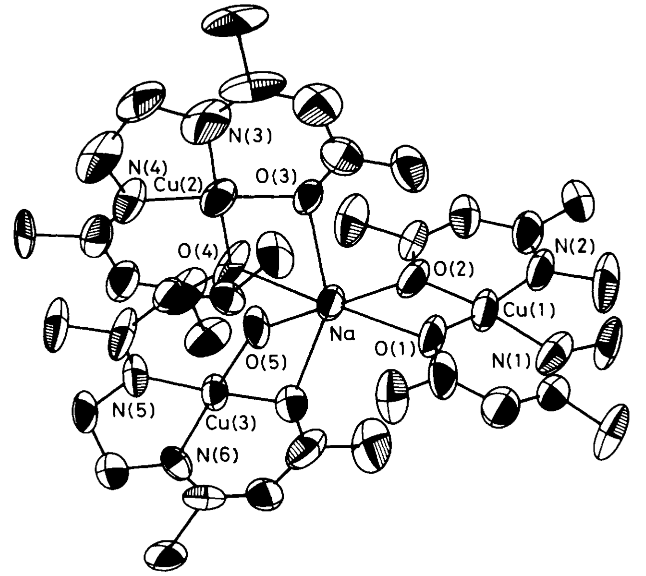


Figure 1. An ORTEP view of the cation $\{[Cu(acacen)]_3Na\}^+$ in complex (**2**). Bond distances (Å): Na–O distances range from 2.36(2) to 2.55(2) Å; Cu–O bond distances from 1.85(1) to 1.95(2) Å; Cu–N bond distances from 1.85(2) to 1.95(2) Å.

with thf and the solution treated with Et_2O gave violet crystals of (**2**) (yield *ca.* 75%).†‡ [See equation (1).] Complex (**2**) has a magnetic moment of 1.78 μ_B at 295 K *per* copper(II) in the structure. Compounds (**3**) and (**4**) have not been characterized.

A view of the cation and anion is shown in Figures 1 and 2 respectively with selected bond distances and angles. The co-ordination around Na^+ is pseudo-octahedral, with the Na–O distances ranging from 2.36(2) to 2.55(2) Å. Sodium is out of the Cu(1), Cu(2), Cu(3) plane by −0.016 Å. The steric crowding around Na^+ due to the bulkiness of the inorganic ligand may be responsible for the differences in the Na–O distances and in the Cu–O bond distances within the [Cu(acacen)] units (see Figure 1). The other structural parameters for [Cu(acacen)] are close to those reported for the free molecule.[8] Complexation of Na^+ by [M(chel)] {chel = salen [*N*,*N*′-ethylenebis(salicylideneiminato)], acacen} complexes has been reported as leading constantly to $\{[M(chel)]_2NaL_2\}$ (L = thf, $\frac{1}{2}ClO_4^-$). This is the first example of a co-ordination cage for Na^+ provided by three metal complex units.[2] Figure 2 shows a picture of the di(benzenethiolato)cuprate(I) anion and a bonding scheme deduced from the structural parameters. Copper(I) has a linear bi-co-ordination [S(1)–Cu(4)–S(2), 178.2(5)°]. The Cu–S bond distances are very close to those observed for bi-co-ordinate copper(I) in $[Cu_5(SPh)_7]^{2-}$[9] and significantly shorter than those observed in some tri-co-ordinate thiocuprates, $[NEt_4]_2[Cu(SPh)_3]$[10] [Cu–$S_{av.}$, 2.250(9) Å] and $[PPh_4]_2[Cu(SPh)_3]$[11] [Cu–$S_{av.}$, 2.295(35) Å]. The Cu–S–Ph bond angles [Cu(4)–S(1)–C(37), 105.0(9); Cu(4)–S(2)–C(43), 105.2(12)°] are similar to those in the complexes mentioned above. The most striking difference between the thiocuprates mentioned above and the anion in complex (**2**) is in the Ph–S bond distances [C(37)–S(1), 1.83(4); C(43)–S(2), 1.63(3) Å], the first one being very close to a C–S single bond and significantly longer than those found in $[NEt_4]_2[Cu(SPh)_3]$[10] [1.758(6) Å] and $[PPh_4]_2[Cu(SPh)_3]$[11] [1.749(14) Å], while the second one approximates a C=S double bond. Such a bond distance is even shorter than those found in $\{[(R_2N)_2C{=}S]_3Cu\}^+$.[12] In addition to that, while the C–C bond distances in the C(37)–C(42) phenyl ring are rather normal, the following C–C bond sequence is observed in the phenyl ring attached to S(2) [C(43)–C(44), 1.44(5); C(44)–C(45), 1.31(6); C(45)–C(46), 1.42(6); C(46)–C(47), 1.51(7);

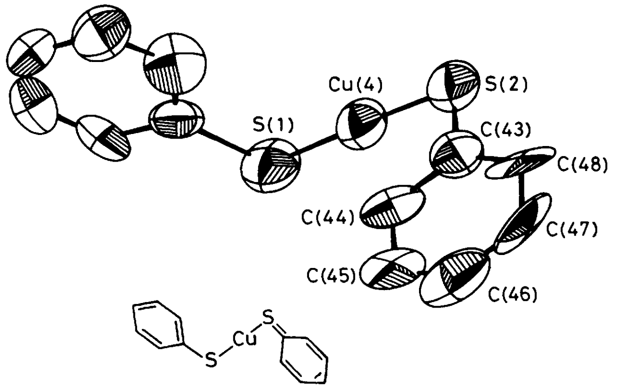
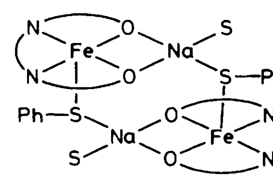
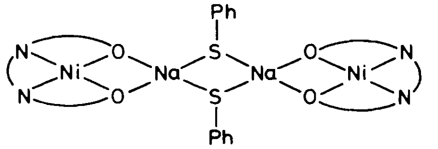


Figure 2. An ORTEP view of the anion $[(PhS)_2Cu]^-$ in complex (**2**). Bond distances (Å): Cu(4)–S(1), 2.142(8); Cu(4)–S(2), 2.154(8); S(1)–C(37), 1.83(4); S(2)–C(43), 1.63(3); C(43)–C(44), 1.44(5); C(44)–C(45), 1.31(6); C(45)–C(46), 1.42(6); C(46)–C(47), 1.51(7); C(47)–C(48), 1.22(6); C(48)–C(43), 1.45(5) Å. Bond angles (°): S(1)–Cu(4)–S(2), 178.2(5); Cu(4)–S(1)–C(37), 105.0(9); Cu(4)–S(2)–C(43), 105.2(12).



(**5**)



(**6**)

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† Complex (**2**) crystallizes with one molecule of thf. Satisfactory analytical data have been obtained.

‡ *Crystal data* for complex (**2**), $C_{52}H_{72}Cu_4NaN_6O_7S_2$: *M* = 1234.47, triclinic, space group $P\bar{1}$, *a* = 11.527(5), *b* = 14.310(3), *c* = 19.285(11) Å, α = 72.16(4), β = 106.97(4), γ = 93.95(3)°, *U* = 2895.6(4) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, λ = 0.71069 Å), *Z* = 2, D_c = 1.416 g cm^{-3}, *F*(000) = 1282. Crystals were mounted in a 0.3 mm Lindemann capillary under nitrogen, $\mu(Mo\text{-}K_\alpha)$ = 15.13 cm^{-1}. Intensity data were collected on a CAD4 diffractometer, θ–2θ scan mode, graphite monochromated Mo-K_α radiation; 6502 independent reflections were measured [(±*h*, ±*k*, *l*); $2 < \theta < 23°$]. The structure was solved by direct methods techniques. Anisotropic blocked matrix least-squares refinement (except for the solvent molecule thf) using unit weights led to an *R* value of 0.0971. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

C(47)–C(48), 1.22(6); C(48)–C(43), 1.45(5) Å]. The structural results seem to justify the bonding scheme reported in Figure 2 for the dithiocuprate. One of the benzenethiolato anions seems to exist in the prevailing carbanionic form, as a consequence of its co-ordination to copper(I). This is a significant result in copper(I)–thiolate chemistry and one which has never been observed either in thiocuprates[9—11] or oxocuprates.[13] Two di(benzenethiolato)cuprate(I) complexes have been reported, $[PPh_4][Cu(SPh)_2]$[10] and $[Et_4N]$-$[Cu(SC_6F_5)_2]$,[14] none of them, however, structurally characterized, while benzenethiolato-cuprates of higher molecular complexity form a very rich class of copper(I) complexes.[9—11,15] A short comment must be added about the genesis of (**2**). Reduction of Cu^{II} to Cu^{I} by PhS^- is a known process[7b] which can, very likely, promote the demetallation of [Cu(acacen)], because of the difference in stability of Cu^{I} in the same ligand environment. The question is, however, how PhSNa can approach the Cu^{II} centre in order to effect the electron transfer. Based on the structures of the compounds formed from the reaction of PhSNa and [M(acacen)] (M = Fe, Ni),[6] an intermediate having the structure of either (**6**) or (**5**) can be suggested for the preliminary stage preceeding the electron transfer.

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