A Study of Copper Compounds by *X*-Ray Absorption Spectroscopy

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Chemical shifts, ΔE, of the *K*-absorption discontinuity in several compounds of copper possessing formal oxidation states between 0 and III have been measured. The shifts show a parabolic dependence on the formal oxidation state as well as on the effective atomic charge, *q*, on copper. Anomalous chemical shifts shown by some of the compounds are discussed in terms of the bonding in these compounds. The ΔE values have also been correlatod with the core electon binding energies obtained from *X*-ray photoelectron spectroscopy.

CHEMICAL shifts of the *K*-absorption discontinuities of transition metals are known to be essentially determined by the oxidation state of the metal in question.[1] We considered it interesting to study copper compounds by *X*-ray absorption spectroscopy (*X*-a.s.) over the entire range of oxidation states between 0 and III, earlier studies [2-5] being limited to oxidation states of I and II. For this purpose we have measured the chemical shifts in a number of oxides, sulphides, halides as well as complexes of copper. Besides correlating the chemical shifts, ΔE, with the oxidation state of copper, we have examined the relation between ΔE and the effective atomic charge,[6] *q*, which for the compounds studied varies between 0 and 1.7. We have also correlated the ΔE values with the core-electron binding energies obtained from *X*-ray photoelectron spectroscopy (*X*-p.s.).

EXPERIMENTAL

The spectra were recorded with a bent-crystal *X*-ray spectrograph. The energy analysis of the spectra was carried out with a Carl-Zeiss G-III rapid photometer. Photometer plots, which represent transmitted intensity as a function of *X*-ray photon energy, were converted into plots of absorption coefficients *vs*. *X*-ray photon energy after determining the photodensities.[7] The position of the absorption edge was taken at the inflection point (midpoint of the steeply rising linear part of the plot) on these photometer records.[8,9] Tungsten impurity lines and copper emission lines were used as references for the measurements, values of the wavelengths of these emission lines being taken from Bearden's tables.[10] The dispersion in the set-up was 12.25 X.U. mm^{-1} on the films and 0.42 X.U. mm^{-1} on the photometer records. Uncertainties in the measurements are within ± 0.5 eV.†

AnalaR samples of Cu[SO$_4$]·5H$_2$O and CuCl$_2$·2H$_2$O were used. All other copper-(I) and -(II) compounds were prepared by standard methods.[11] Copper(II) sulphide was prepared by heating a stoicheiometric mixture of the elements in a sealed evacuated tube at 670 K for 1 d followed by quenching the sample to room temperature. Copper(I) sulphide was prepared by heating high-purity copper powder in a stream of H_2S at 920 K followed by slow cooling in H_2S. The trivalent copper compounds K[Cu(biuret)$_2$] and $Ba_2Cu_2O_5$ were prepared by methods reported in the literature.[12,13] For the latter compound, chemical analysis revealed that *ca*. 90% copper was in the III state. The zero-valent copper compounds [Cu(PPh$_3$)$_2$] and K$_2$[Cu(pc)]·*x*NH$_3$ (where pc = phthalocyaninate) were prepared by methods reported in the literature.[14,15]

RESULTS AND DISCUSSION

In the Table we have listed the energy corresponding to the *K*-absorption discontinuity of copper in a number of compounds, along with the chemical shift, ΔE. The data are plotted against the formal oxidation state in Figure 1. We can readily see that the so-called zero-valent copper compounds [14,15] [Cu(PPh$_3$)$_2$] and K$_2$[Cu(pc)]·*x*NH$_3$ exhibit finite but small chemical shifts considerably less than 1 eV. It appears that, although the effective charge on copper may not actually be zero in these compounds, the formal oxidation state is likely to be close to zero since ΔE in compounds with Cu in oxidation state I is generally around 2.5 eV. The small ΔE values of the copper(0) compounds also show that higher oxidation states of copper, if present as impurities, are only in small concentrations. The present results lend support to the first report by Layton *et al.*[14] that [Cu(PPh$_3$)$_2$] is a copper(0) compound and allay the doubt expressed by these authors in a later paper.

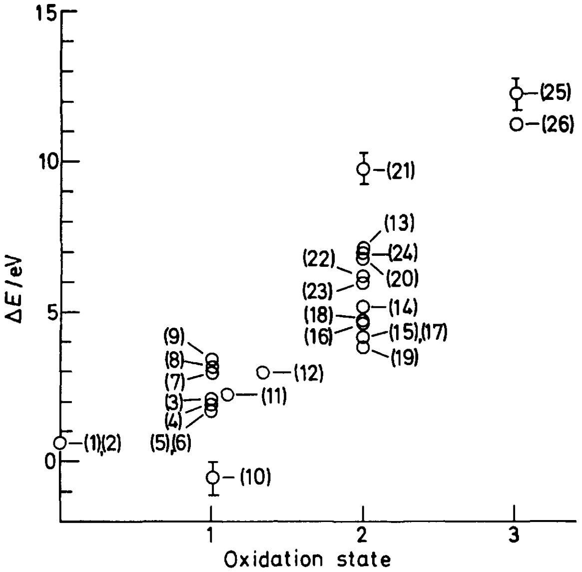

FIGURE 1 Plot of chemical shift, ΔE, against the formal oxidation state of copper for compounds listed in the Table. The uncertainty in ΔE values (± 0.5 eV) is indicated in three cases

Almost all of the copper(I) compounds give chemical shifts in the range 2.5 ± 0.5 eV. Exceptions are Cu_2O and copper(I) cyanides. The oxide gives a small negative shift (−0.55 eV) in agreement with an earlier

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

Chemical shifts of Cu *K*-absorption discontinuities in copper compounds

	Compound	Formal oxidation number	Energy,[a] E/eV $\pm$ 0.5	Chemical shift,[b] ΔE/eV	Effective charge on Cu, q
(1)	$[Cu(PPh_3)_2]$	0	8 979.87	0.62	(0.15)
(2)	$K_2[Cu(pc)]\cdot xNH_3$	0	8 979.82	0.57	(0.14)
(3)	CuCl	1	8 981.35	2.10	0.59
(4)	CuBr	1	8 981.23	1.98	0.39
(5)	CuI	1	8 981.03	1.78	0.18
(6)	$[Cu(PPh_3)_3]I$	1	8 981.05	1.80	(0.41)
(7)	Cu[SCN]	1	8 982.25	3.00	(0.65)
(8)	$K[Cu(CN)_2]$	1	8 982.35	3.10	(0.67)
(9)	Cu[CN]	1	8 982.65	3.40	(0.71)
(10)	Cu_2O	1	8 978.70	0.55	
(11)	Cu_9S_5	1.11	8 981.49	2.24	0.53
(12)	CuS	1.33	8 982.25	3.00	0.61
(13)	$CuF_2\cdot 2H_2O$	2	8 986.35	7.10	1.21 [c]
(14)	$CuCl_2\cdot 2H_2O$	2	8 984.47	5.22	1.06 [c]
(15)	$CuBr_2\cdot 2H_2O$	2	8 983.44	4.19	0.48 [c]
(16)	$Cs[CuCl_3]$	2	8 983.96	4.71	0.79
(17)	CuO	2	8 984.42	4.17	1.12
(18)	[Cu(pc)]	2	8 984.04	4.79	(0.96)
(19)	La_2CuO_4	2	8 983.13	3.88	1.22
(20)	$Cu[SO_4]\cdot 5\ H_2O$	2	8 986.03	6.78	(1.27)
(21)	$[Cu(O_2CMe)_2]\cdot H_2O$	2	8 989.85	9.80	
(22)	$[Cu(C_2O_4)]\cdot 0.5H_2O$	2	8 985.45	6.20	
(23)	$Cu(BO_2)_2$	2	8 985.25	6.00	(1.16)
(24)	$[Cu(NH_3)_4(SO_4)]\cdot H_2O$	2	8 986.20	6.95	(1.30)
(25)	$K[Cu(biuret)_2]$	3	8 991.55	12.30	
(26)	$Ba_2Cu_2O_5$	3	8 990.63	11.38	1.68

[a] E_{edge} (Cu metal) = 8 979.25 $\pm$ 0.50 eV. [b] Chemical shift $\Delta E = E_{edge}$ (compound) $- E_{edge}$ (metal). [c] Charge calculated for anhydrous compound.

report,[16] but this shift is close to experimental error. This compound exhibits a unique cubic structure in which copper has a linear oxygen co-ordination involving mainly $3d_{z^2}$–$4s$ hybrid orbitals with a relatively small contribution from $4p$.[17] The energy of the *K*-absorption edge, which corresponds to the difference between the $1s$ level and the first unoccupied level having $4p$ character, is nearly the same in Cu_2O and Cu metal perhaps because the metal $4p$ orbitals are not involved in the bonding of Cu_2O. In Cu[CN] and $K[Cu(CN)_2]$ we find a slightly larger ΔE than in other copper(I) compounds probably because of d_π–p_π back bonding between copper and cyanide which would increase the effective charge on the metal atom. In copper(I) sulphide, having the composition Cu_9S_5, copper has an average oxidation state of +1.11 and accordingly we find a ΔE of 2.24. For CuS we have taken the formal oxidation state of the metal to be +1.33, since it is a mixed-valence compound,[18] $Cu^{2+}(Cu^+)_2S^{2-}(S_2^{2-})$, ΔE in this compound does indeed fall between that characteristic of copper-(I) and -(II) compounds (Table).

All the copper(II) compounds give chemical shifts in the range 5.5 $\pm$ 1.6 eV (Table). The only exception to this is copper(II) acetate monohydrate which has metal–metal interaction. It was pointed out earlier[19] that copper(II) carboxylates with metal–metal bonds show large chemical shifts. The additional positive shift in the *K* edge may arise from copper–copper interaction[20] and the associated destabilisation of the metal $4s$ and $4p$ levels. It is interesting that La_2CuO_4, which has metallic properties,[21] shows the lowest ΔE.

We have been able to study two compounds with copper in the formal oxidation state III, $K[Cu(biuret)_2]$ and $Ba_2Cu_2O_5$, and the chemical shifts in these are around 11.8 $\pm$ 0.5 eV. In spite of the deviations exhibited by some of the compounds, an examination of Figure 1 shows that the plot of ΔE against oxidation state is parabolic. The parabolic relation becomes evident only because of the experimental points for copper-(0) and -(III) compounds, otherwise one can mistake the relation to be linear.

It has been found worthwhile to correlate chemical shifts with effective charge, q, on the absorbing atom rather than with valency, number of electrons, ionicity, and similar parameters.[6] The q values obtained by the method of Suchet[22,23] have been found to be useful in

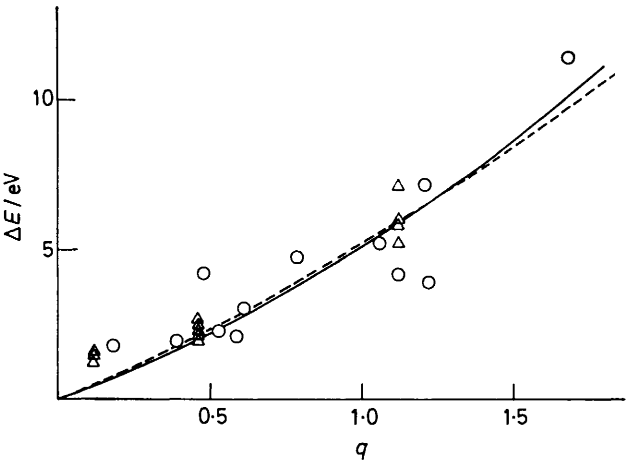

FIGURE 2 Plot of chemical shift, ΔE, of copper compounds against the effective atomic charge, q. The circles refer to our experimental data and the triangles to data given in ref. 3. The solid curve is obtained by least-squares fit of our data and the dotted curve by least-squares fit of data including those taken from ref. 3

this regard. According to Suchet, q is given by equation (1) where Z, r, and n are respectively the total number of

$$q = n\{1 - 0.011\,85[(Z/r') + (Z'/r)]\} \qquad (1)$$

electrons, ionic radius, and oxidation state of the cation. The primed symbols refer to the corresponding values of the anion. In Figure 2 we have plotted the experimental ΔE of 12 of the relatively ionic compounds studied by us against q (Table). The data could be fitted to expression (2), where $a = 3.64$ and $b = 1.37$

$$\Delta E = aq + bq^2 \qquad (2)$$

and with a standard deviation of 1.28. We have also calculated the regression line including ΔE data of 13 other compounds reported by Ballal and Mande.[3] This provides a least-squares fit with $a = 4.13$ and $b = 0.78$ and standard deviation 1.06. The parabolic nature of the ΔE–q plots in Figure 2 is similar to that found in Figure 1, where ΔE was plotted against the formal oxidation state of copper. Having found a relationship between ΔE and q, we can, in principle, estimate q in those copper compounds where Suchet's formula is not directly applicable. Although such estimates of q are subject to some uncertainty (*ca.* 0.2), we have listed them in parentheses for some of the compounds (where q values may be meaningful) in the Table. From these estimates we see that q in the copper(0) compounds is around 0.15. The ΔE of copper(II) acetate monohydrate is much higher than predicted by the ΔE–q relation; other carboxylates with metal–metal bonding are similarly associated with high ΔE values.

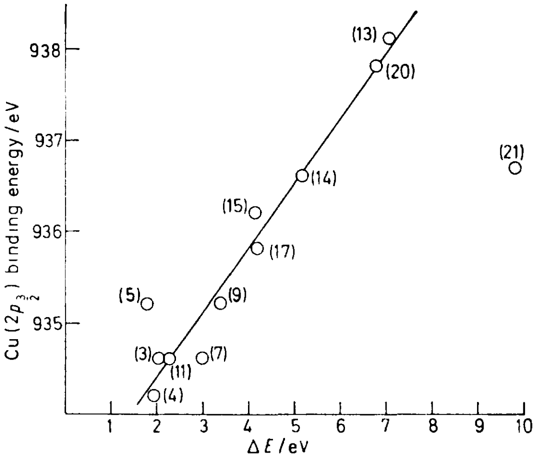

FIGURE 3 Plot of chemical shift, ΔE, of copper compounds listed in the Table against Cu($2p_{\frac{3}{2}}$) binding energy from X-ray photoelectron spectroscopy

In Figure 3 we have correlated the ΔE values with the Cu ($2p_{\frac{3}{2}}$) binding energies obtained from X-ray photoelectron spectroscopy.[24] A linear relation is obtained, from which copper(II) acetate again shows a large deviation. This relation lends some support to the implicit assumption made in this study that ΔE is related to the charge on the metal atom or its ionicity.

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