Inorganica Chimica Acta, *179* (1991) 113–115

An XPS study of poly-bis(μ-di-n-alkylphosphinato)copper(II) compounds

Hongliang Hu, Jing-Long Du, Robert C. Thompson* and David C. Frost*
Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Y6 (Canada)

(Received May 2, 1990; revised August 17, 1990)

Abstract

X-ray photoelectron spectroscopic (XPS) studies are reported on nine poly-copper(II) di-n-alkylphosphinates, $Cu[(C_nH_{2n+1})_2PO_2]_2$ (where $n=2$, 4 and 6 and two polymorphs each of the compounds where $n=8$, 10 and 12). While there is very little variation in the $C(1s_{1/2})$, $O(1s_{1/2})$ and $P(2p_{3/2})$ binding energies (BEs) amongst the nine compounds, significant differences are seen in the $Cu(2p_{3/2})$ and $Cu(2p_{1/2})$ BEs. These latter BEs are discussed in relation to the known structures and magnetic properties of these materials.

Introduction

Studies on di-n-alkylphosphinates of copper(II), $Cu[(C_nH_{2n+1})_2PO]_2$, have revealed some rather unique magneto–structural relationships. Compounds where $n/2=1$–6 may be classified into distinct α and β forms, the former exhibiting antiferromagnetic behaviour and the latter ferromagnetic [1–3]. Whereas each of the compounds with $n=2$, 4 and 6 have been obtained in only one form, the $n=8$, 10 and 12 compounds exhibit polymorphism and are obtainable in both forms [3]. Single crystal X-ray diffraction studies on the antiferromagnetic C_2 compound [1] (α form) and the ferromagnetic C_4 [4] and C_6 [2] compounds (β form) show all three to be polymers with structures involving well-separated infinite chains of eight-membered rings, each made up of two copper atoms (compressed tetrahedral, D_{2d}, symmetry) bridged by two phosphinate groups. Of the three compounds, the ethyl derivative has the most compressed CuO_4 chromophore and differs from the other two in regard to the orientation of the alkyl groups relative to the eight-membered rings, the latter affecting the nature of the interchain packing [2]. It has been suggested also that similar structural differences characterize the α and β forms of the C_8, C_{10} and C_{12} derivatives and that differences in the detailed geometries of the CuO_4 chromophores, in particular, account for the differences in the magnetic properties of the two forms [3]. Both ferromagnetic and antiferromagnetic pathways for exchange (involving overlap of the magnetic orbital with primarily σ- and π-type ligand orbitals, respectively) are considered to be available for these compounds with a flattening of the CuO_4 chromophore favoring the latter pathway.

Although several X-ray photoelectron spectroscopic (XPS) studies have been made on diamagnetic and magnetically dilute paramagnetic materials [5–7], similar attention has not been paid to magnetically concentrated materials. We report here detailed XPS studies on the nine poly-copper(II) di-n-alkylphosphinates described above. We were particularly interested in determining whether any of the measured binding energies could be correlated with the structural form (α or β) and therefore with magnetic type (antiferromagnetic or ferromagnetic). Moreover, since inner core binding energies reflect to some extent electron delocalization effects involving valence electrons, it was hoped to obtain through these studies a better understanding of the differences in the electronic and magnetic properties of these materials. Although there have been a number of studies on metal phosphinate compounds in recent years [8] this represents the first systematic XPS study on these interesting compounds.

Experimental

Procedures used to prepare the compounds have been described previously [1–3]. XPS data were

---

*Authors to whom correspondence should be addressed.

0020-1693/91/$3.50

obtained using a Varian IEE-15 spectrometer with Mg Kα X-rays as the exciting radiation ($h\nu = 1253.6$ eV). The samples were studied as fine powders thinly dusted onto Scotch Tape 3M, and binding energies referred to the C 1s level of graphite, 284.0 eV [9].

Results and discussion

XPS binding energies (BEs) are given in Table 1. Each measurement was repeated with a fresh sample (except for the β-C_{12}, compound where only one measurement was made), and the data in the Table represent the averages. In most cases the BEs were, when repeated, within 0.1 eV and in no case were they more than 0.2 eV different.

We consider first the results obtained for the C_8, C_{10} and C_{12} compounds where for each one both α and β forms are available. Earlier it was shown that the two forms of these compounds have distinctive electronic and vibrational spectra as well as thermal and magnetic properties [3]. To this we can now add distinctive XPS features. The C($1s_{1/2}$), O($1s_{1/2}$) and P($2p_{3/2}$) BEs tend to be slightly higher in the α forms compared to the β forms although the difference in general barely exceeds the experimental uncertainty. For Cu, however, the α forms exhibit $2p_{3/2}$ BEs from 0.2 to 0.6 eV higher than the corresponding β forms while the difference is even greater for the $2p_{1/2}$ BEs, ranging from 0.7 to 1.0 eV. The spin–orbit separations ($2p_{1/2}$–$2p_{3/2}$) range from 0.2 to 0.8 eV higher in the α compounds. The higher BEs as well as spin–orbit separations in the α compounds suggest greater 2p electron localization around the copper atoms compared to that in the β compounds [5]. These XPS results clearly show that the most significant difference in inner shell BEs between the α and β forms involves the metal, which is consistent with an earlier observation [3] that one of the more important structural differences between the two forms involves the detailed copper stereochemistry — the degree of compression of the CuO_4 chromophore. If we assume that the more compressed CuO_4 chromophore in the α molecules results in greater metal to ligand 3d electron delocalization (perhaps mainly via π orbitals on the ligands) this would result in an increased nuclear charge on the metal and account for the increased BE of the inner shell electrons. In addition, while increased 3d electron delocalization will result in a decrease in spin–orbit coupling for the 3d electrons, the increased nuclear charge will have the effect of contracting the inner 2p orbitals and increasing the spin–orbit coupling associated with them (as we observe) [10].

The C_2, C_4 and C_6 compounds are each available in only one form and hence a one-to-one comparison between two forms of the same compound is not possible for these. We note as before that the most informative XPS features for these compounds involve the Cu($2p_{3/2}$) and Cu($2p_{1/2}$) BEs. In particular, the C_4 and C_6 compounds both exhibit Cu($2p_{1/2}$) BEs and spin–orbit separations very comparable to those of the β-C_8, C_{10} and C_{12} compounds, consistent with their classification as β forms. For the C_2 compound both the Cu($2p_{1/2}$) BE and the spin–orbit separation are greater than for the β compounds again consistent with its classification as an α compound. In this case, however, the Cu($2p_{1/2}$) BE is significantly greater (~ 1 eV) than those of the other α compounds indicating even greater metal to ligand 3d electron delocalization.

The question as to whether the extent of 3d electron delocalization as reflected by the Cu($2p_{1/2}$) BEs correlate with the compounds' magnetic properties can only be partly answered. The five β compounds (ferromagnetic with relatively weak, magnetic coupling, J values ranging from 1.8 to 2.3 cm^{-1}) exhibit relatively less 3d electron delocalization than the α-

TABLE 1. Inner-shell binding energies

Compound	Binding energies (eV)				
	Cu($2p_{1/2}$)	Cu($2p_{3/2}$)	C($1s_{1/2}$)	O($1s_{1/2}$)	P($2p_{3/2}$)
α-$Cu[(C_2H_5)_2PO_2]_2$	955.4	935.0	285.1	531.2	132.8
β-$Cu[(C_4H_9)_2PO_2]_2$	953.8	935.0	284.9	531.2	132.6
β-$Cu[(C_6H_{13})_2PO_2]_2$	953.7	934.9	284.8	530.9	132.4
α-$Cu[(C_8H_{17})_2PO_2]_2$	954.5	935.2	285.1	531.1	132.6
β-$Cu[(C_8H_{17})_2PO_2]_2$	953.5	935.0	284.3	530.6	131.3
α-$Cu[(C_{10}H_{21})_2PO_2]_2$	954.4	935.2	285.0	531.1	132.7
β-$Cu[(C_{10}H_{21})_2PO_2]_2$	953.6	934.7	284.7	530.9	132.5
α-$Cu[(C_{12}H_{25})_2PO_2]_2$	954.3	935.1	284.8	531.1	132.5
β-$Cu[(C_{12}H_{25})_2PO_2]_2$	953.6	934.6	284.7	530.8	132.4

C_8, C_{10} and C_{12} compounds (antiferromagnetic with relatively strong magnetic coupling, $|J|$ values ranging from 25 to 29 cm^{-1}). While the extent and type of exchange appears to be related to the extent of 3d electron delocalization in these eight compounds, the correlation is not general as seen by the results for the C_2 compound. This compound exhibits the greatest 3d electron delocalization of the compounds studied (highest Cu ($2p_{1/2}$) BE yet, while it does exhibit antiferromagnetism, the magnitude of the exchange is relatively weak ($|J| = 1.3$). The explanation for this probably lies in the fact that, while the XPS results reflect the effects of 3d electron delocalization generally, the magnetic properties are influenced primarily by metal–ligand interactions involving the metal orbital containing the unpaired electron (the magnetic orbital). Hence while 3d electron delocalization arising from interaction with ligand π orbitals may in fact be less overall for the α-C_8, C_{10} and C_{12} compounds compared to that for the C_2 compound, it is possible that the orientation of the ligand π orbitals in the former group of compounds is such as to provide greater interaction with the magnetic orbital. Confirmation of this could come from single-crystal X-ray diffraction studies; unfortunately none of the phosphinates of copper which show strong antiferromagnetic coupling have as yet been obtained in a crystalline form suitable for such studies.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and K. Oliver for samples of previously prepared compounds.

References

1 K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem., 60* (1982) 2017.

2 J.S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem., 62* (1984) 891.

3 J. S. Haynes, K. W. Oliver and R. C. Thompson, *Can. J. Chem., 63* (1985) 1111.

4 R. Cini, P. Colamarino, P. L. Orioli, L. S. Smith, P. R. Newman, H. D. Gillman and P. Nannelli, *Inorg. Chem., 16* (1977) 3223.

5 D. C. Frost, C. A. McDowell and I. S. Woolsey, *Chem. Phys. Lett., 17* (1972) 320.

6 C. S. Fadley and D. A. Shirley, *Phys. Rev. A, 2* (1970) 1109.

7 J. C. Carver, T. A. Carlson, L. C. Cain and G. K. Schweitzer, in D. A. Shirley (ed.), *Electron Spectroscopy*, North-Holland, Amsterdam, 1972, p. 803.

8 P. Betz and A. Bino, *Inorg. Chim. Acta, 147* (1988) 109, and refs. therein.

9 K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren and B. Lindberg, *ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almquist and Wiksells, Boktryckeri, AB, 1965, p. 225.

10 D. C. Frost, A. Ishitane and C. A. McDowell, *Mol. Phys., 24* (1972) 861, and refs. therein.