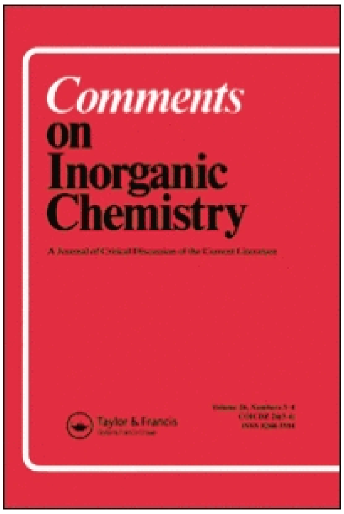

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Photoelectron Spectroscopy of Metal Dithiocarbamate, Xanthate and Dithiophosphate Complexes: A Review

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Photoelectron Spectroscopy of Metal Dithiocarbamate, Xanthate and Dithiophosphate Complexes: A Review

1. SCOPE

The chemistry of the metal dithiocarbamates and related complexes has been extensively reviewed previously. The book, *The Dithiocarbamates and Related Compounds* by Thorn and Ludwig[1] is generally recognized as the classic reference text for metal dithiocarbamate chemistry. Very broad and detailed reviews on transition metal (including lanthanides and actinides) and nontransition metal dithiocarbamates and xanthates have been published by Coucouvanis,[2,3] which concisely discuss synthesis, spectroscopic data, magnetic moments, x-ray structural data and adduct synthesis and characterization. The analytical chemistry of metal dithiocarbamates and related compounds has been extensively reviewed by Magee[4] and very recently by Magee and Hill.[5] These reviews discuss in detail the electroanalytical, separatory, radiochemical, thermoanalytical, spectroscopic, mass spectrometric, titrimetric and ion-selective electrode aspects of these complexes. The electrochemistry and redox behavior of transition metal dithiocarbamates have been comprehensively reviewed by Bond and Martin[6] and the thermochemistry of metal dithiocarbamates, metal xanthates

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and metal dithiophosphates has been reviewed by Hill and Magee[7] with emphasis on thermal decomposition mechanisms of these complexes, as derived by thermal analysis techniques in conjunction with mass spectrometry and the solution thermochemistry leading to metal–ligand bond energies. Sengupta and Kumar[8] have published a short, incomplete review of some thermal analysis data for metal dithiocarbamate complexes.

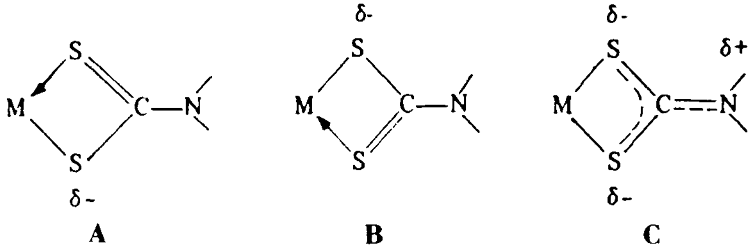
McCormick, Bereman and Baird[9] have reviewed the synthetic methods and structures of transition metal (including lanthanides and actinides) and nontransition metal monothio- and monoselenocarbamate complexes and Mehrotra, Srivastava and Chauhan[10] have reviewed the chemistry of dialkyldithiophosphate derivatives of nontransition metals. Haiduc[11] and Wasson *et al.*[12] have independently reviewed the chemistry of metal dithiophosphate complexes.

From a careful study of the content of these reviews, it is apparent that the x-ray photoelectron spectroscopic (XPS) data for metal dithiocarbamates and related complexes have not been collectively discussed previously in detail. XPS (or ESCA) is attracting increasing interest as a very useful and versatile structural technique in coordination chemistry and correlations between XPS binding energies and various physical properties of transition metal complexes have been identified, which are of major significance in the understanding of metal–ligand interactions. Thus, the scope of this review encompasses x-ray photoelectron spectroscopic data for transition and nontransition metal dithiocarbamate, monothiocarbamate, xanthate and dithiophosphate complexes. Correlations of relevant XPS binding energies with a variety of physical properties are discussed with specific reference to the structures and chemical properties of these complexes.

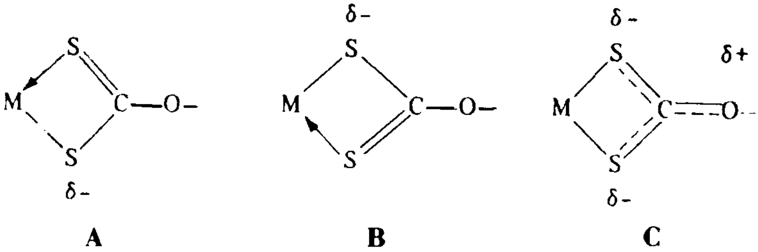
2. INTRODUCTION

A. Metal Dithiocarbamate, Xanthate and Dithiophosphate Chemistry

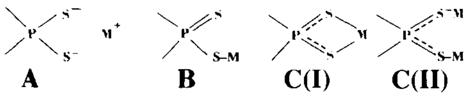
Metal dithiocarbamates $[R_2NCS_2]_lM$, metal xanthates $[ROCS_2]_mM$ and metal dithiophosphates $[(RO)_2PS_2]_nM$ (R is alkyl or aryl) form a large group of chemically similar and structurally related complexes. The chemistry of these systems is largely explained on the basis of the interaction between the metal and various canonical forms of the ligand[1-3]:



Dithiocarbamates



Xanthates



Dithiophosphates

together with the superimposed inductive effect of the terminal R-groups. It is generally accepted[1-3] that the canonical form of type C features predominantly in the rationalization of the chemistry of these systems.

In coordination chemistry, much interest is centered on the degree of metal–ligand interaction and thus metal dithiocarbamate, xanthate and dithiophosphate complexes have been intensively studied using techniques such as infrared,[5] UV-visible spectroscopy,[5] electron spin resonance[5] and, to a limited extent, x-ray[13] and UV photoelectron spectroscopy.[14] Relatively recent electrochemical studies[6] have considerably augmented knowledge of the metal environment in these complexes and thermoanalytical studies[7] have indicated the degree of thermal stability and thermal decomposition mechanisms for a wide variety of such complexes.

It appears that the available PES data for these complexes has not been fully exploited, since it is increasingly evident that XPS binding energies, as related to the coordinated metal or ligand donor atoms, may be linearly correlated with, for example, infrared stretching/rocking frequencies, g_{11} tensors (ESR), thermochemical metal–ligand bond energies, electrochemical metal $E_{1/2}$ values and d-d transition energies. It is this aspect of the PES data for metal dithiocarbamate, xanthate and dithiophosphate complexes that is investigated and discussed in this review.

B. The Technique of X-Ray Photoelectron Spectroscopy (XPS)

Photoelectron (or photoemission) spectroscopy (PES) involves the study of electrons ejected from atoms, molecules, liquids or solids due to photon impact. The energy of the incident photons determines the approximate upper limit of binding energy for those electrons which are just able to be ejected. Consequently, a study of the kinetic energy distribution of photoemitted electrons reflects the occupancy of bound electronic states for a material. This energy analysis may be performed by a variety of spectroscopic techniques, each of which produces a photoelectron spectrum of kinetic energies—an XPS spectrum, if x rays are used.

Following the accepted explanation by Einstein[15] in 1905, photoemission in subsequent studies has followed an interesting historical path.[16] The most productive phase began in the 1950s and 1960s with the work of Siegbahn *et al.* in Uppsala, Sweden.[17,18] Many excellent reviews have also been written concerning the technique of which[19–21] are representative.

A convenient one-dimensional description of the photoemission process is shown in Fig. 1 and represents what is known as the "three-step model" of photoemission: (i) photoionization of an atom inside the sample in which a bound electron gains energy

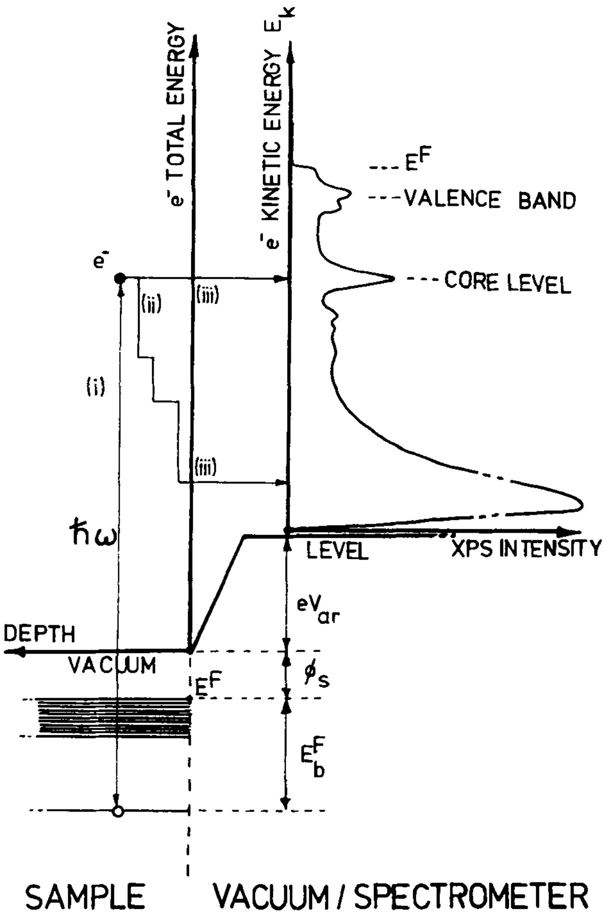


FIGURE 1 Schematic photoemission is shown in terms of the three-step model. In particular, excitation of a one-dimensional metal sample is shown for a core-level electron (energy increase $\hbar\omega$), at some depth in the sample followed by transport of this electron towards the vacuum due to its kinetic energy. Such electrons emerge either (a) as "no-loss" electrons, provided they are close to the surface, and contribute to the core level spectral peak or (b) as scattered electrons having suffered inelastic collision(s) before emission. The accelerating/retarding potential V_{ar} is applied to the photoelectrons as a sweeping voltage to tune their energy to that of the energy analyzer of the spectrometer. φ_s is the spectrometer work function (Ref. 8).

$\hbar\omega$, (ii) transport (including scattering) of these electrons through the sample, especially transport in directions towards the sample surface, and (iii) escape of the electrons through the surface potential barrier into vacuum where measurement can be made of their kinetic energy distribution. Other, more sophisticated models have also been proposed.[19–21]

A schematic energy distribution of a photoelectron spectrum is as shown in Fig. 1. Principal features include: (a) A large low kinetic energy peak, comprising greater than 95% of all the photoelectrons, and which arises as a result of the energy losses which take place in inelastic scattering events in step (ii). (b) A cutoff or spectral edge at high kinetic energy, limited by the photon energy size. For metal samples this corresponds to emission of Fermi surface electrons. (c) Various peaked structures at intermediate kinetic energies which arise from: electrons in bound states escaping without energy loss (unscattered), energy loss peaks associated with such peaks (plasmons, shake-up, shake-off), multiplet structures, exchange splittings, Auger electrons and others. Each atomic species in a sample contributes such a characteristic set of atomic-like core levels and associated peaks. In approximate terms, the XPS spectrum reflects the occupied density of bound states together with these ancillary features.

Much XPS research has involved a study of what are called chemical shifts. These arise because a given core level on a given elemental atom has a binding energy which depends on the chemical environment of the atom. The measurement of such shifts may be made relative to standard compounds or complexes containing a given atom or may be made from direct measurements of binding energy (E_b^F relative to the Fermi level E^F) from Fig. 1; for example,[22]

$$E_b^F = \hbar\omega - E_k - eV_{ar} - \varphi_s.$$

The intensity of a core level spectral peak depends, apart from instrumental and transport/escape factors, upon: the photon intensity, the concentration N of a given atom/core level type in the sample and the photon-core level ionization cross section $d\sigma/d\Omega$.[19–21] This essentially involves a dipole matric element between the initial core level and the final quasifree electron states in the sample as well as asymmetry and angular effects (involving the relative direction between photon and electron paths). Approximately, the area A under a core level peak is given by:

$$A \propto N\sigma\lambda$$

where λ is the mean free path for such electrons corresponding to their transport, no-loss kinetic energy in the sample.

The width of spectral features is the result of convolution of the energy analyzer resolving "window" with the causal width produced as a result of the processes leading to ejection of a particular type of electron (core level, Auger, etc.)

Chemical shifts may be interpreted in various ways. One of the simplest involves the assignment of effective atomic charges in a given molecule arising from fractional bond ionicities. These charges then have the "potential" to change the binding energy of core electrons on atoms.

Such atomic charges have also been shown to have an effect on interatomic vibrational frequencies. Chemical shifts may as a result be correlated with shifts in vibrational (stretching, rocking) frequencies in molecules.[23,24]

The correlation of binding energies and their chemical shifts with other physical/chemical parameters has also been researched; for example, with cation oxidation states in metal oxides,[25] with oxidation number and d-orbital occupancy,[26,27] with Mössbauer isomer shifts[28-31] with NQR (Cl^{35}),[32,33] with thermochemical energies,[34] and with g_{11} in ESR measurements.[35]

Since binding energy data relate directly to the electronic environment of an atom in a molecule, PES is an invaluable technique for investigating metal–ligand interaction in coordination complexes. The chemistry of metal dithiocarbamates, xanthates and dithiophosphates is extensive and has been well documented, and for this group of structurally related complexes, there exists copious physical data for potential correlation with existing PES data for these complexes. Thus a review of such PES data provides a premise for comment on the significance of PES as a prime structural probe in coordination chemistry.

3. SUMMARY OF PES DATA FOR METAL DITHIOCARBAMATE, XANTHATE AND DITHIOPHOSPHATE COMPLEXES

Walton[36] has published a very brief review of the x-ray photoelectron spectra of metal dithiocarbamate, xanthate and dithiophosphate complexes up to 1980. For metal dithiocarbamates, it is apparent that the S 2p binding energies occur in the relatively narrow range of 162.9–161.7 eV and show no obvious correlation with the nature of the coordinated metal ion. These S 2p binding energies are very similar to those of other low oxidation state sulfur ligands and thus Walton[36] concludes that the S 2p binding energy range for metal dithiocarbamate complexes is of little diagnostic value. Walton[36] further suggests that the occurrence of satellites at about 6 eV above the S 2p main lines for metal dithiocarbamates may be due to "in-situ" formation of high oxidation state sulfur contaminants. From S 2p binding energy data available for metal xanthates and dithiophosphates, Walton[36] concludes that since the S 2p binding energies for metal dithiocarbamates, xanthates and dithiophosphates are very similar, S 2p XPS studies on complexes containing any combination of these ligands are unlikely to reveal more than a broadened S $2p_{1/2,3/2}$ doublet.

Frost *et al.*[37] have reported an extensive XPS study of metal diethyldithiocarbamate complexes: $M(Et_2dtc)_3$: M = Fe(III) and Co(III), and $M(Et_2dtc)_2$: M = Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). For these complexes, the N 1s, S 2p and S 2s binding energy ranges are 400.1–400.4 eV, 162.5–162.9 eV and 226.3–226.8 eV, respectively. These compare with 399.9 eV, 161.7 eV and 225.8 eV, respectively, for sodium diethyldithiocarbamate. The order of average metal–sulfur bond lengths for the first row transition metal dithiocarbamate complexes studied is $Fe > Co > Ni < Cu < Zn$, which is opposite to the trend in corresponding N 1s, S 2p and S 2s binding energies. Frost *et al.*[37] conclude that these data are consistent with the trend in metal–ligand bond strengths, since the smaller the coordinate bond length, the greater the overlap between metal and ligand and the greater the electron deficiency of the ligand orbitals. Metal $2p_{1/2}$, 3s and 3p satellites were observed for Fe(III), Co(III), Ni(II) and Cu(II) diethyldithiocarbamates and S 2p satellites were observed additionally for

Zn(II), Pb(II), Cd(II), Hg(II), Ag(I) and Na(I) diethyldithiocarbamates. These satellites are interpreted in terms of ligand ↔ metal charge transfer transitions via correlations with corresponding UV absorption spectroscopic data. Also, the valence region of the XPS data for these complexes was interpreted qualitatively using molecular orbital data.

Kramer and Klein[38] have presented a Fe 3p XPS binding energy (chemical shift) scale for a series of Fe compounds including Fe(III) diethyldithiocarbamate (Fig. 2). Within the series selected, Fe(III)

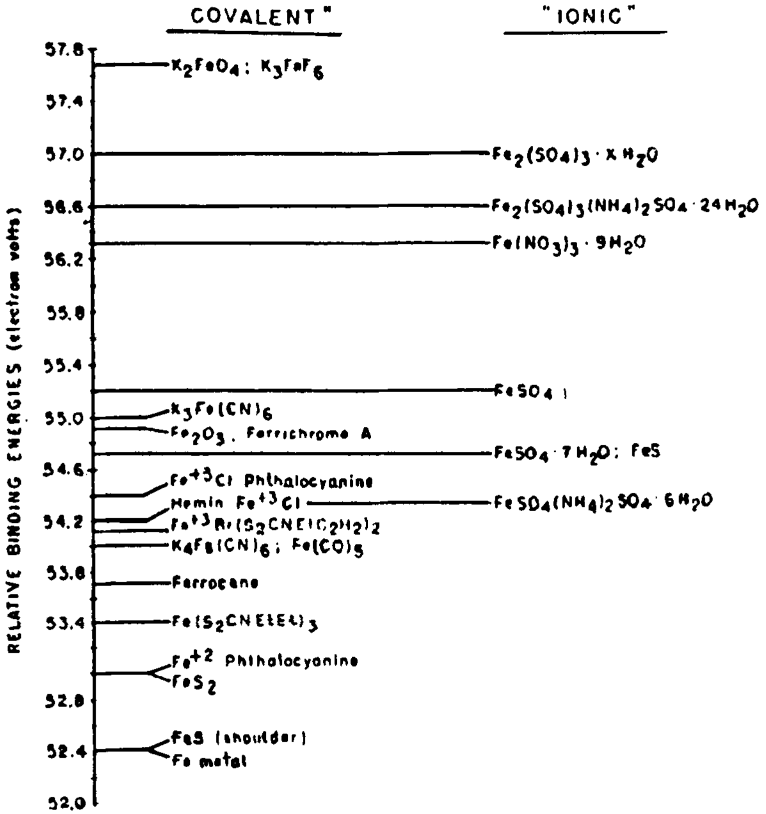


FIGURE 2 Chemical shifts of the Fe 3P electron binding energy in Fe compounds.

diethyldithiocarbamate is considered a covalent compound, since a relatively low Fe 3p binding energy (53.4 eV) is exhibited. From these data, it is apparent that XPS is a useful technique for differentiating between ionic and covalent complexes.

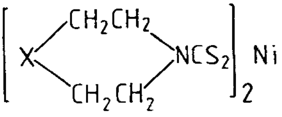
Best *et al.*[39] have reported S 2p binding energies for a series of transition metal dithiocarbamate complexes: $Fe[S_2CN(C_2H_5)_2]_3$, $Fe(NO)[S_2CN(CH_3)_2]_2$, $Fe(NO)[S_2CN(C_2H_5)_2]_2$, $Co[S_2CN(CH_3)_2]_3$, $Mo(NO)_2[S_2CN(C_2H_5)_2]_2$, $Mo(NO)[S_2CN(C_2H_5)_2]_3$ and $Mo_2O_4[S_2CN(C_2H_5)_2]_2$ which group within the narrow range of 161.7–163.1 eV. XPS S 2p binding energies are thus of little value in a structure analysis of such complexes.

Cauletti *et al.*[14] have reported He(I) UV photoelectron spectra (UPS) for a series of iron(II) dithiocarbamate dicarbonyl complexes of general type $Fe(Dtc)_2(CO)_2$, which under the experimental conditions employed, decompose via loss of carbon monoxide and thus behave as bis(dithiocarbamato)iron(II) complexes. Substituent effects due to terminal methyl, ethyl or phenyl substituents attached to the nitrogen of the dithiocarbamate moiety are reflected as a decrease in the relevant binding energies for these complexes, in the order $(\text{aromatic})_2 < (\text{aromatic})(\text{aliphatic}) < (\text{aliphatic})_2$ and are explained in terms of the relative degrees of π-electron delocalization within the coordination sphere.

Haraguchi *et al.*[40] have reported the Co 2p, N 1s and S 2p binding energies for cobalt(III) dithiocarbamates: $(R_2NCS_2)_3Co$: R = Me, Et, and Co 2p and S 2p binding energies for cobalt(III) xanthates: $(ROCS_2)_3Co$: R is Et, Pr. All these complexes exhibit satellite lines and on the basis of the XPS data, it is not possible to differentiate between dithiocarbamate and xanthate complexes of Co(III).

Nefedov and Zhumadilov[41] have reported the Ni $2p_{3/2}$ binding energies for bis(diethyldithiocarbamato)nickel(II) and bis(di-*n*-butyldithiophosphato)nickel(II) as 854.4 eV and 854.8 eV, respectively. Thus, on the basis of XPS data it is not possible to differentiate between dithiocarbamate and dithiophosphate complexes of nickel(II) complexes containing ligands with O, N, S and Se donor atoms. Nefedov and Zhumadilov[41] have shown that a correlation exists between the Ni($2p_{3/2}$) binding energy and g_{11} (ESR) for such a series of complexes.

Furlani *et al.*[42] have reported extensive XPS data for a series of heterocyclic nickel(II) dithiocarbamates:



where X is CH_2 (piperidinedithiocarbamate = pipdtc), HN (piperazinedithiocarbamate = pzdtc), H_3CN (N-methylpiperazinedithiocarbamate = Mepzdtc), O (morpholinedithiocarbamate = morphdtc), S (thiomorpholinedithiocarbamate = timdtc).

The Ni $2p_{3/2}$ and S 2p binding energies for these complexes are within the ranges 854.0 ± 0.1 eV and 162.5 ± 0.3 eV, respectively. Thus, it appears that the $[NiS_4]$ chromophore is little effected by the nature of the remote substituent X as is expected for saturated heterocyclic metal dithiocarbamate complexes.

Frost *et al.*[35] have reported Cu $2p_{3/2,1/2}$, Cu 3s and Cu 3p binding energies for a wide variety of copper(II) complexes including bis(diethyldithiocarbamato)copper(II). For the latter complex, Cu $2p_{3/2}$, Cu $2p_{1/2}$, Cu 3s and Cu 3p binding energies are 934.0 eV, 954.1 eV, 123.6 eV and 76.3 eV, respectively. For the series of square-planar copper(II) complexes studied, a correlation was shown to exist between core-level binding energies and g_{11} (ESR). Satellite lines in the XPS spectrum of bis(diethyldithiocarbamato)copper(II) were explained in terms of ligand → metal 3d or ligand → ligand* transitions.

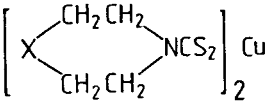
Ioffe and Borod'ko[43] have made a detailed study of the satellite structure associated with the XPS spectra of a series of copper(II) complexes including bis(diethyldithiocarbamato)copper(II) and a correlation is shown to exist between satellite intensities and the copper spin density α^2 as obtained from ESR data. Thus, it is concluded that such satellite fine structure arises exclusively from excitation of the copper unpaired electron.

Thomson *et al.*[44] have reported XPS data for a wide variety of copper(II) complexes including bis(diethyldithiocarbamato)-copper(II) and have discussed satellite structure in terms of optical absorption data. Significant "in-situ" photoreduction of Cu(II) → Cu(I) was noted in the XPS analysis of these complexes.

Chang and Cheng[45] have reported C 1s, N 1s, and S 2p binding energy data for Cu(II), Pb(II) and Sn(IV) diethyldithiocarbamates.

Also, Cu $2p_{3/2}$, Pb $4f_{5/2,7/2}$ and Sn $3d_{5/2}$ binding energies are reported for the respective complexes. The XPS data for these complexes indicate three carbon environments and one sulfur environment, consistent with bidentate binding of the diethyldithiocarbamate ligand to the metal in each case. It is not possible to differentiate between these complexes on the basis of C 1s, N 1s and S 2p binding energies in view of the narrow ranges exhibited.

Furlani *et al.*[46] have reported extensive XPS data for a series of heterocyclic copper(II) dithiocarbamates:



where X = CH_2, S, NH, NCH_3 and O. Cu $2p_{3/2}$, Cu 3p, S 2s, S 2p, N 1s and C 1s binding energies are given for these complexes and a linear correlation is shown to exist between the relative intensity of the Cu $2p_{3/2}$ satellite peaks and the magnetic moments of the complexes as show in Fig. 3.

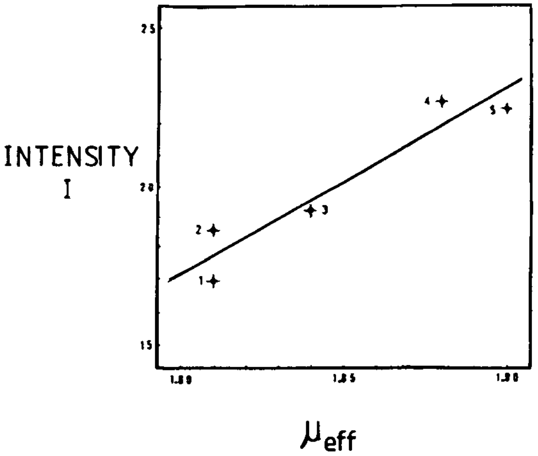


FIGURE 3 Plot of total satellite intensity (ratio of the corresponding satellite area to the total area cf satellite + the main line $Cu2p_{3/2}$) versus μ_{eff}. (1) $Cu(Pipdtc)_2$, (2) $Cu(Timdtc)_2$, (3) $Cu(Mepzdtc)_2$, (4) $Cu(Morphdtc)_2$, (5) $Cu(Pzdtc)_2$.

On the basis of the XPS data, it is apparent that the [CuS_4] chromophore in these complexes is little effected by the nature of the remote heterocyclic substituent X which is further substantiated by UPS data for Cu(pipdtc)$_2$ and Cu(Morphdtc)$_2$, which exhibit He(I) bands at 810 and 833 eV, respectively. However, it appears that the intensity of associated satellite lines is dependent on the nature of X.

Sodovskii and Larionov[47] have reported x-ray absorption *K* spectra for Fe(III), Co(III), Cr(II), Ni(II), Zn(II), Sb(III) and Cd(II) ethylxanthates and Co(III), Ni(II), Cu(II) and Zn(II) diethyldithiocarbamates. The spectra are consistent with bidentate binding of xanthate and dithiocarbamate ligands to the metal and extensive metal → ligand d electron delocalization.

Zumandilov *et al.*[48] have reported XPS spectra for a series of metal diamyldithiocarbamates: $(R_2NCS_2)_nM$: R = Amyl: $n = 2$; M = Ni(II), Cu(II), Cd(II) Zn(II) or Pd(II): $n = 3$; M = Co(III) or Sb(III) and for a series of metal di-*n*-butylthiophosphates $[(BuO)_2 PS_2]_n$ M: $n = 2$; M = Ni(II), Cu(II), Zn(II), Cd(II), Ba(II) or Pb(II): $n = 3$; M = Co(III), Sb(III) or Bi(III). The binding energy data are consistent with extensive metal–ligand, d electron delocalization in these complexes.

Payne *et al.*[13] have reported M $2p_{3/2}$, and S 2p binding energies for a series of nickel(II) and copper(II) diethyldithiocarbamate complexes $(R_2NCS_2)_2M$: M = Ni(II) or Cu(II); R = H, CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, cyclohexyl, morpholyl, piperidyl or pyrrolydyl. A linear correlation is shown to exist between N 1s and S 2p binding energy shifts and the N-C and M-S infrared stretching frequencies $\bar{f}$ for the nickel and copper dithiocarbamate complexes, respectively, as shown in Fig. 4. A theoretical justification of the observed correlation is presented, based on a very detailed theoretical model for XPS binding energy/infrared stretching frequency correlations developed by Liesegang and Lee.[23]

Payne *et al.*[49] have extended their previous XPS study to include a series of nickel(II) xanthate complexes, $(ROCS_2)_2Ni$: R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9 or *i*-C_4H_9. The Ni $2p_{3/2}$ and S 2p binding energy shifts for these complexes are shown to exhibit linear correlations with the corresponding Ni-S infrared stretching frequencies and the correlations are rationalized in terms of the variation in inductive effect of the terminal R group of the xanthate

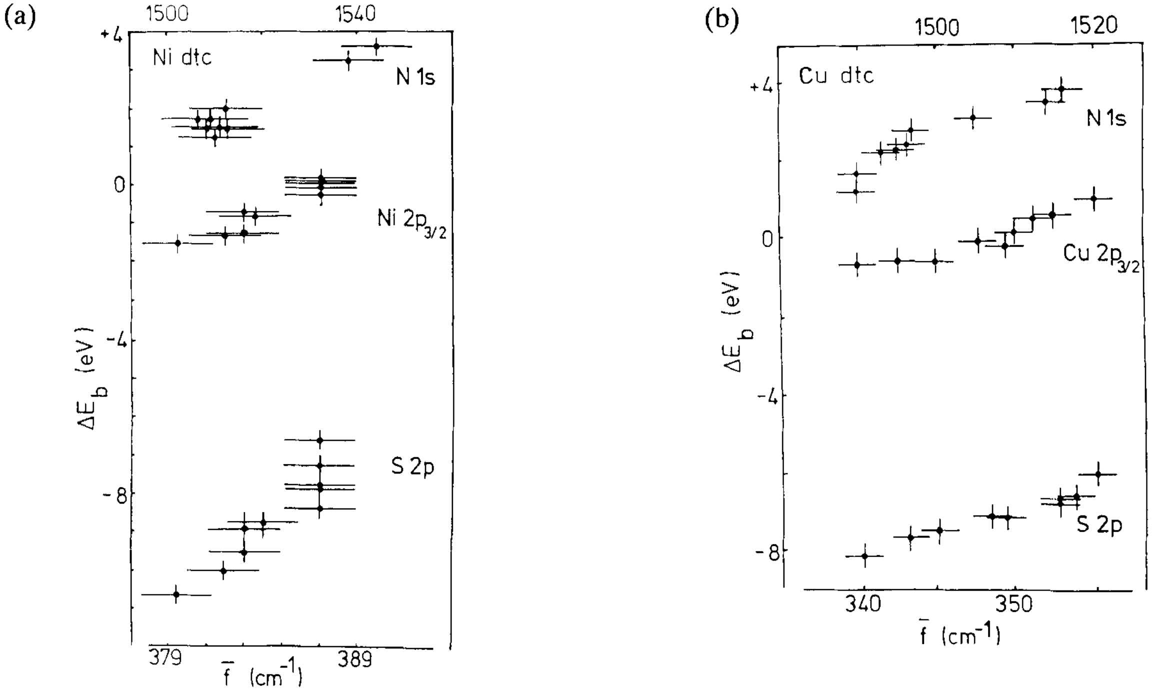


FIGURE 4 Variation in core-level binding energy E_b (for the levels indicated) with stretching frequency $\bar{f}$ for (a) Ni(II) and (b) Cu(II) dithiocarbamates with various R-groups. The upper and lower $\bar{f}$ scales refer to C-N and M-S stretching frequencies, respectively.
]

moiety. These correlations are shown in Figs. 5 and 6 together with corresponding correlations for the series of nickel dithiocarbamate complexes previously studied. A theoretical argument is presented by Liesegang and Lee[23] to account for the opposite slopes of pairs of xanthate and dithiocarbamate correlations, which relates to the relative magnitude of the charges on the metal and the donor sulfur atoms in these complexes.

Larsson *et al.*[50] have reported XPS data for N-cyanodithiocarbamate complexes of Ni(II), Pd(II) and Pt(II) and the data were

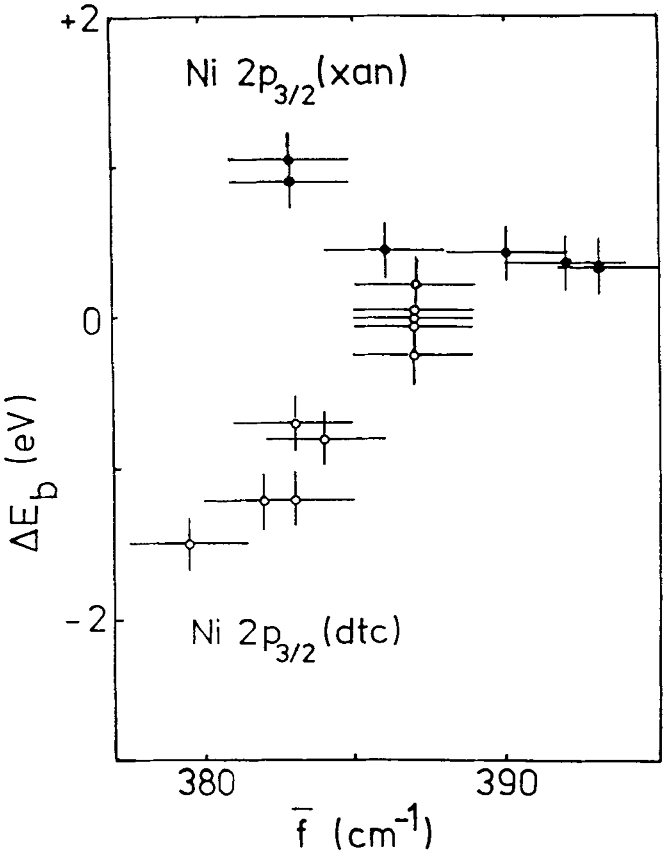


FIGURE 5 Variation of Ni $2p_{3/2}$ core-level binding energy shift in xanthates (●) and dithiocarbamates (○) with Ni-S stretching frequency $\bar{f}$.

correlated with corresponding infrared and Raman spectroscopic data for these complexes. Atomic charge calculations for these complexes further revealed that qNi > qPd > qPt, which is consistent with a decreasing metal–ligand bond strength within this Ni triad series of complexes.

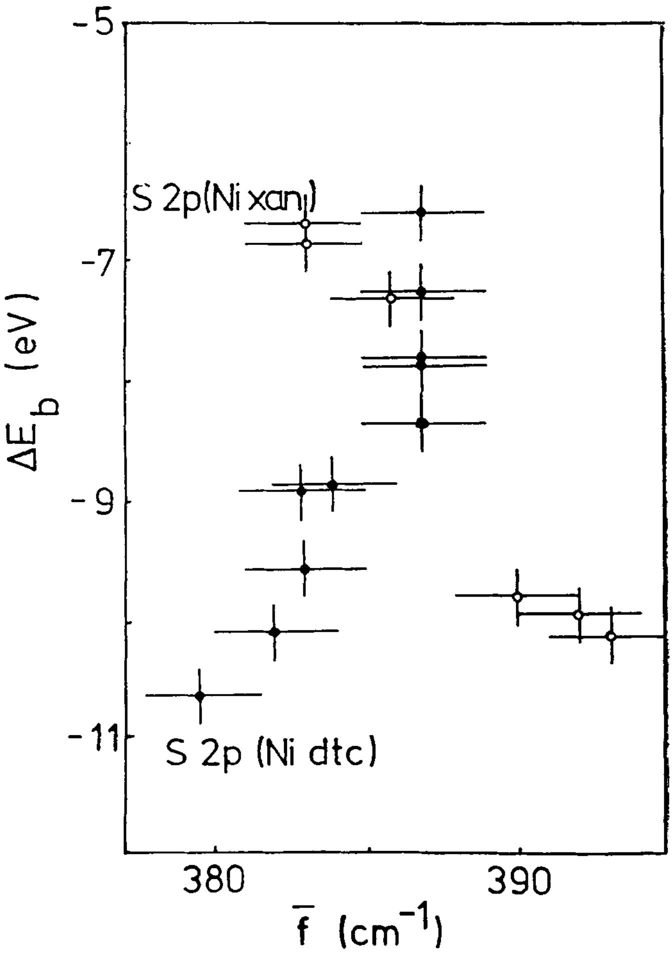


FIGURE 6 Variation of the S 2p core level binding energy shift in Ni(II) xanthates (○) and dithiocarbamates (●) with Ni-S stretching frequency $\bar{f}$.

Baranovskii *et al.*[51] have reported Rh $3d_{5/2}$, S 2p and N 1s binding energies for tris(diethyldithiocarbamato)rhodium(III) as 308.9 eV, 162.6 eV and 400.0 eV, respectively. The S 2p and N 1s binding energies for these complexes are within the expected range for metal dithiocarbamate complexes.

Willemse *et al.*[52] have applied XPS to characterize bis(di-*n*-butyldithiocarbamato)platinum(II) and to differentiate between the two geometrical isomers of [bis(di-*n*-butyl-dithiocarbamato)diiodo]platinum(IV). However, the brown and red forms of the latter complex give an identical S 2p XPS spectrum with one broad band at 165 eV. The S 2p binding energy for $(Bu_2NCS_2)_2Pt$ is 164 eV. Thus XPS binding energies for ligand atoms are of no value for the differentiation of geometrical isomers of corresponding complexes.

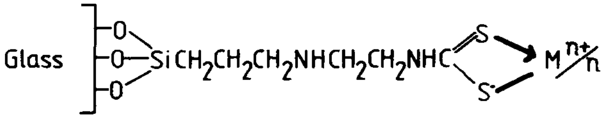
Van Attekum and Trooster[53] have studied two gold(III) dithiocarbamate complexes by XPS: $[AuMe_2(S_2CNMe_2)]$ and $[AuBr_2(S_2CN\textit{n}\text{-}Pr_2)]$. The stability of these complexes is studied as a function of sample preparation technique, temperature and x-ray intensity. "In-situ" photoreduction of these complexes yields gold(I) dithiocarbamate complexes and it was found that the rate of such decomposition is substantially reduced by using graphite as substrate and by reducing the sample temperature. Furthermore, the binding energy of the 4f-core levels of these gold(III) dithiocarbamate complexes is strongly dependent on the ligand group electronegativity consistent with predominantly ionic metal–ligand bonding.

Perry and Geanangel[54] have reported Sn $3d_{3/2}$, Sn $3d_{5/2}$, S $2p_{1/2}$, S $2p_{3/2}$ binding energies for two tin(II) dithiocarbamates: $(R_2NCS_2)_2Sn$: R = CH_3, C_2H_5. The difference betwen corresponding binding energies for this complex is ±1 eV and hence an assessment of the relative electronic effects of the terminal alkyl groups of the dithiocarbamate moiety on the tin coordination sphere is not possible.

Walton[55] has reported Tl $4f_{5/2}$, Tl $4f_{3/2}$ and N 1s binding energies for tris(diethyldithiocarbamato)thallium(III) as 122.8 eV, 118.4 eV and 399.5 eV, respectively. These data are discussed in terms of the "softness" of the dithiocarbamate ligand by comparison with ligands such as heterocyclic tertiary amines, the thallium chloride derivatives of which exhibit higher Tl 4f binding energies.

Boyer *et al.*[56] have applied XPS to study the structure of $[PhTl(CH_2S_2CNMe_2)\ (S_2CNMe_2)]$. The data are consistent with thallium exhibiting coordination number 4 extensive π-electron delocalization over metal and ligands.

Hercules *et al.*[57] have adapted PES for use in trace metal analysis by using glass fiber mats with chelating groups attached to their surfaces, thereby effectively creating selective "scavengers" for metal ions from aqueous media. This type of surface was produced by treating glass fibers with an amino functional silylizing reagent and subsequently with carbon disulfide and sodium hydroxide to form a "fixed" dithiocarbamate, which subsequently complexes with heavy metals as shown schematically by:



Detection limits of the order of 10 ppb were noted for lead, calcium, thallium and mercury. The PES–glass fiber disk technique in trace metal analysis represents a unique application of photoelectron spectroscopy.

4. COMMENTS AND CORRELATIONS

The majority of the PES data cited in this Comment refer to first row transition metal dithiocarbamate, xanthate and dithiophosphate complexes. There is little PES data available for the corresponding complexes of other transition metals and nontransition metals. Furthermore, for the metal dithiocarbamates, the majority of the available PES data refer to the diethyl-derivative. Thus, it is difficult to discuss and classify the overall PES data in terms of the traditional periodic and group trends.

A summary chart showing the metals for which PES data exist for the corresponding dithiocarbamate, xanthate and dithiophosphate complexes is presented in Fig. 7.

Despite the overall paucity of PES data for these complexes, and the difficulty that different referencing procedures have been used in obtaining such data, some general comments can be made

DITHIOCARBAMATES								
	Fe(III)	Co(III)	Ni(II)	Cu(II)	Zn(II)			
Mo(VI)		Rh(III)	Pd(II)	Ag(I)	Cd(II)		(II) Sn(IV)	Sb(III)
			Pt(II)	Au(III)	Hg(II)	Tl(III)	Pb(II)	
XANTHATES								
Cr(II)	Fe(III)	Co(III)	Ni(II)		Zn(II)			
					Cd(II)			Sb(III)
DITHIOPHOSPHATES								
		Co(III)	Ni(II)	Cu(II)	Zn(II)			
					Cd(II)			Sb(III)
							Pb(II)	Bi(III)

FIGURE 7 Summary chart showing the metals for which PES data exist for the corresponding dithiocarbamate, xanthate and dithiophosphate complexes.

relating the experimental binding energy shifts to the chemistry of metal dithiocarbamates, xanthates and dithiophosphates.

The reported XPS data are consistent with the dithiocarbamate, xanthate or dithiophosphate binding to metals as a bidentate ligand and the sulfur donor atoms of these ligands are indistinguishable, which is consistent with extensive π-electron delocalization within the [MS_n] chromophore. Ligand binding energy shifts are of little value to differentiate between different dithiocarbamate complexes or to distinguish between dithiocarbamate, xanthate and dithiophosphate complexes. The origin of satellites associated with the XPS spectra of these complexes is incompletely understood. "In-situ" photoreduction appears to be a consistent feature of XPS studies of copper(II) dithiocarbamates, xanthates and dithiophosphates, and "in-situ" decomposition has been shown to occur during XPS analysis of iron(II) dithiocarbamate dicarbonyl complexes, which is possibly a common feature of complexes of the type $M(dtc)_2L_2$ where L is a weakly bound neutral ligand in the axial position. PES data for a variety of metal dithiocarbamate, xanthate and dithiophosphate complexes have revealed that terminal R-groups on the ligand exert a considerable electronic effect on the $[MS_n]$ chromophore but not when substituents are part of a terminal heterocyclic ring. Finally, the PES data for these complexes generally confirm extensive π-electron delocalization within the $[MS_n]$ chromophore, thereby suggesting strong metal–ligand interaction.

In terms of correlations of XPS data with other physical parameters, correlations have been shown to exist between experimental binding energies and the calculated charges on atoms,[18] calculated chemical shifts,[18] the oxidation number of a metal in a complex,[26,27] Mössbauer chemical shifts[28–31] nuclear quadrupole resonance frequencies,[32,33] g_{11} ESR parameters,[35] infrared stretching frequences[23] and infrared rocking frequences.[24]

For metal dithiocarbamate or xanthate complexes, correlations have been shown to exist between experimental binding energies and g_{11} ESR parameters[41] magnetic moments,[46] infrared stretching frequencies[13] and Raman spectroscopic transitions.[50] With reference to the XPS data presently reviewed, it is possible to investigate further correlations on a limited basis.

For the diethyldithiocarbamate complexes of Ni(II), Cu(II) and Zn(II), the metal ($2p_{1/2}$) binding energies, referenced to the C 1s level (285.0 eV) are 872.0, 953.6 and 1047.2 eV, respectively.[37] A plot of these binding energies versus metal atomic number is shown in Fig. 8. A linear correlation results which is consistent with a decreasing metal–sulfur bond energy of the diethyl-dithiocarbamate complex with increasing atomic number of the metal. Thermochemical homolytic metal–sulfur bond energies, as derived from solution calorimetric data for Ni(II) and Cu(II) diethyldithiocarbamate complexes are 193 and 143 kJ, respectively,[58,59] which are in accord with the XPS data for these complexes. Trends with respect to variation of the ligand are not apparent from corresponding XPS data, in the case of either transition metal or non-transition metal dithiocarbamate, xanthate or dithiophosphate complexes as is revealed from the sets of data in Table I.

Correlations between XPS and electrochemical data for metal dithiocarbamates are also apparent but complexes for which comparable sets of data are available are limited. For example, Ahmed and Magee[60] have reported an extensive chronopotentiometric study

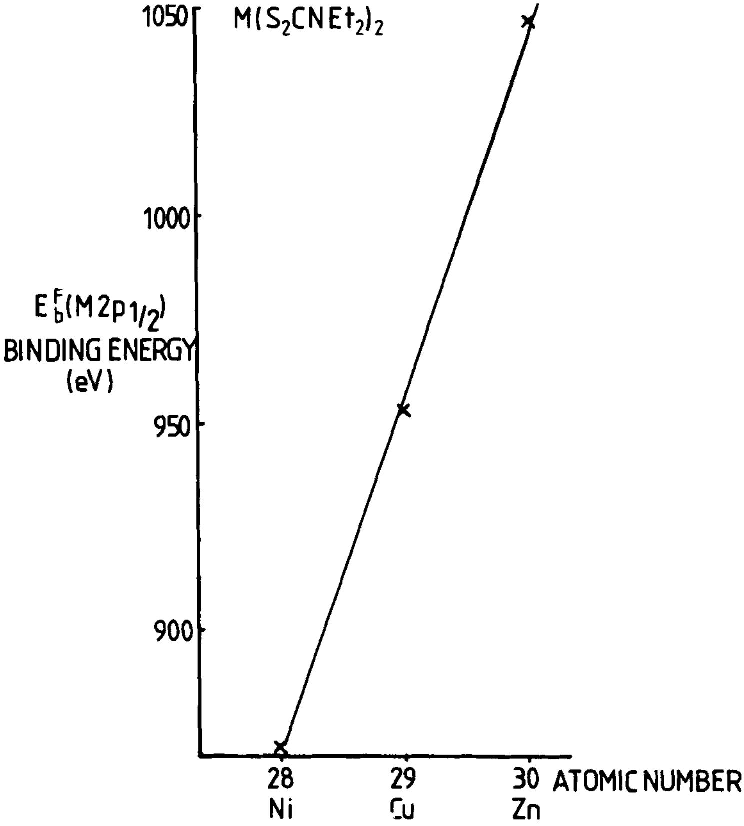


FIGURE 8 Correlation of E_b^F (M $2p_{1/2}$) binding energies: $M(S_2CN\,Et_2)_2$ M = Ni, Cu, Zn, with atomic number.

on a wide range of nickel(II)dithiocarbamate complexes and polarographic reduction potentials E_p and Ni ($2p_{3/2}$) binding energy shifts ΔE_b (relative to E_b (Cu metal) ($2p_{3/2}$) = 932.5 eV[61]) for corresponding complexes are tabulated in Table II and plotted in Fig. 9.

A linear correlation exists between E_p and ΔE_b (Ni $2p_{3/2}$) for this limited series of complexes. Both E_p and ΔE_b parameters are related to the electronic environment of the coordinated metal, and within a series of structurally related complexes, this environ-

TABLE I

	E_b M($2p_{3/2}$) eV	Reference
$Co(Me_2NCS_2)_3$	779.5	40
$Co(Et_2NCS_2)_3$	779.4	40
$Co(EtOCS_2)_3$	779.2	40
$Co(n\text{-}PrOCS_2)_3$	778.8	40
$Ni(Et_2NCS_2)_2$	854.4	37
$Ni[(n\text{-}BuO)_2PS_2]_2$	854.8	41
$Sn(Me_2CS_2)_2$	163.3	54
$Sn(Et_2CS_2)_2$	163.1	54

ment changes due to a progressive change in the inductive effect of the terminal R groups attached to the dithiocarbamate moiety and hence changes in E_p and ΔE_b are both reflecting the change in inductive effect of these R groups as manifested in the resulting change of the electronic environment of the metal center.

It is thus apparent that a variety of further correlations of XPS data with other physical parameters are feasible for metal dithiocarbamate, xanthate and dithiophosphate complexes, but in view of the limited sets of comparable data available, the interpretations of such correlations are at present speculative.

5. CONCLUSIONS

Following this Comment on the application of PES to study metal–sulfur-containing ligand complexes, it is of interest to contemplate

TABLE II

$Ni(S_2CNR_2)_2$ R	E_p[60] (volts)	ΔE_b Ni $2p_{3/2}$[49] (eV)
H	−1.13	−1.57
Me	−1.02	−1.29
Et	−0.76	−0.86
n-Bu	−0.55	−0.32

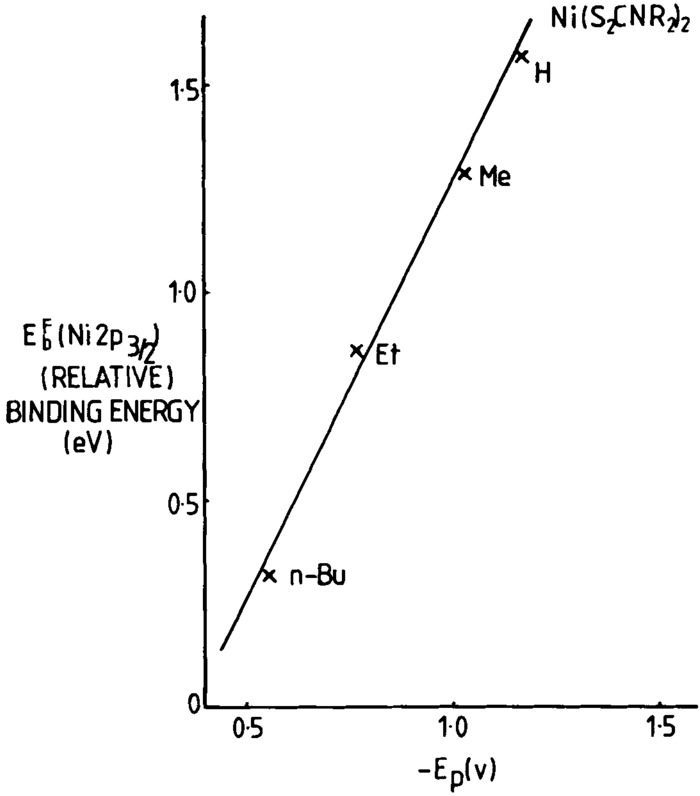


FIGURE 9 Correlation of polarographic reduction potentials, E_p with E_b^F (Ni 2p$_{3/2}$) binding energies for bis(*n*-alkyldithiocarbamato)nickel(II) complexes: Ni(S$_2$CN R$_2$)$_2$: R = H, Me, Et, *n*Bu.

on the future of this technique in inorganic chemistry in general and in coordination chemistry in particular. In this respect, Cowley[62] has reviewed the application of UV photoelectron spectroscopy in the structural analysis of a wide variety of organometallic complexes such as metal carbonyls, nitrosyls and alkyls and has concluded that UVPS has considerable potential for differentiating between ionic and covalent complexes and for comparison of metal–ligand bond strengths in a series of complexes of similar structure. For the metal dithiocarbamates, xanthates and dithiophosphates, PES is of some value in the detection of finer structural effects such as those resulting from change of terminal R-group substituents, introduction of other ligands such as carbon monoxide or nitric oxide and change in oxidation state of the coordinated metal. However, although binding energy shifts, multiple splitting phenomena and "shake-up" satellites have been reported for a wide variety of metal dithiocarbamates, xanthates and dithiophosphates, the structural significance of such data is not always self-evident. Comparison of XPS data for the same complex from different sources is made complicated by the different calibration and referencing procedures used, and this factor alone may invalidate any trends identified in such data. There is an identified need for standardization of referencing procedures in PES.

This Comment has shown that there are many advantages in a PES study of a series of closely related complexes such as the metal dithiocarbamates, xanthates and dithiophosphates. These complexes exhibit a wide range of terminal R-group substituents, which may be straight-chain, branched-chain or part of a heterocyclic ring and such complexes involving a wide variety of transition and nontransition metals are known. The majority of available PES data for these complexes refer to relatively few elements and predominantly to the corresponding dimethyl- and diethyl-derivatives. Following standardization of referencing procedures, a binding energy shift scale according to metal oxidation state and R-group substituent can be developed for these complexes. Also, for a series of structurally related complexes, trends in metal binding energy shifts for such complexes with respect to progressive change in metal atomic number across a period and down a group can be investigated. It is expected that such periodic trends will reflect the normal double periodic variation, which has been shown to exist for core-level binding energies of first row transition metals.[63]

The group trends should be consistent with an increasing degree of ionic character associated with these complexes with increasing metal atomic number along with some rationalization of the degree of metal–ligand π-bonding. For dithiocarbamate, xanthate or dithiophosphate complexes involving the same coordinated metal, the corresponding XPS data need to be refined in order to elucidate trends based on a progressive change of the terminal R-group substituents. For the xanthate series of complexes, an XPS investigation of adduct formation is suggested.

The linear correlations of XPS binding energies and other physical parameters already identified can be extended to include correlations with other infrared data such as rocking vibrations, with g_{11} values generally and with electronic, metal d-d transitions and metal–ligand charge transfer transitions, as obtained from UV-visible spectroscopic data. With respect to the latter, correlations of XPS satellite transitions and metal d-d and metal–ligand CT transitions also need further investigation. The potential of PES as an analytical technique appears promising in view of the glass fiber technique developed by Hercules[57] and the wide variety of dithiocarbamate terminal groups which can be attached to the fiber surface.

There is clearly much scope for the further application of PES to metal dithiocarbamate, xanthate and dithiophosphate chemistry.

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