Inorg. Chem. **1992**, *31*, 2281–2282

Table I. Size and Potential Parameters[a] of Molecular Anions

	radius params, Å				potential params, au			
ion (basis) (energy, au)	$\bar{r}^{b}$	$r_<$	$r_>$	Δr	$\bar{V}$	$V_<$	$V_>$	ΔV
BH_4^- (tz2p) (−26.985)	1.73 (1.79^h)	1.58	2.29	0.38	−0.249	−0.262	−0.217	0.011
OH^- (tz2p) (−75.376)	1.14 (1.19^h)	1.07 (1.33^b)	2.03 (1.40^c)	0.17	−0.396	−0.441	−0.184	0.060
CN^- (tz2p) (−92.326)	1.52 (1.77^h)	1.33 (1.91^b)	1.89	0.17	−0.277	−0.320	−0.256	0.013
N_3^- (tz2p) (−163.313)	1.75 (1.81^h)	1.64 (1.95^b)	2.38	0.19	−0.233	−0.280	−0.205	0.026
NO_2^- (tz2p) (−204.132)	1.62 (1.78^h)	1.26	2.23	0.23	−0.270	−0.319	−0.206	0.028
NO_3^- (tz2p) (−279.004)	1.88 (1.65^h)	1.75 (1.89^c)	2.47	0.16	−0.224	−0.281	−0.177	0.032
SH^- (dz2p) (−398.067)	1.62 (1.93^h)	1.53 (2.07^b)	3.01 (1.95^c)	0.15	−0.286	−0.312	−0.171	0.031
BF_4^- (tz2p) (422.877)	2.00 (2.18^h)	1.84 (2.28^c)	2.54	0.18	−0.228	−0.240	−0.198	0.010
CNS^- (tzp)[c] (−489.864)	2.27 (1.99^h)	1.63 (1.95^c)	3.18	0.53	−0.209	−0.249	−0.151	0.025
ClO_3^- (tzp) (−683.862)	2.09 (1.57^h)	1.83 (1.71^b)	2.65 (2.00^c)	0.20	−0.207	−0.276	−0.136	0.048
ClO_4^- (tzp) (−758.668)	2.21 (2.26^h)	2.10 (2.40^b)	2.73 (2.36^c)	0.15	−0.210	−0.234	−0.172	0.016
BrO_3^- (G-1) (−2796.339)	2.24 (1.40^h)	1.91 (1.91^c)	2.77	0.19	−0.195	−0.269	−0.121	0.052

[a] See text for details. [b] The values in parentheses denote the Huheey[3] (h) and Marcus[16a] (b), and Marcus[16c] (c) thermochemical (spherical) radii, respectively. The values in the top line are the present (spherically averaged) ones. [c] The literature radii for the SCN^- ion are from refs 3 and 16c, respectively, for comparison.

It is also possible to unearth further "chemical" information from the parameters derived from MESP maps. For instance, one may make qualitative predictions of anisotropies in electrostatic interactions of these ions with interacting ions/molecules. The low values of ΔV for CN^- and ClO_4^- (cf. Table I) imply that these species would not be significantly anisotropic with respect to such interactions. This is in accordance with the recent thermodynamic studies which have led to the conclusion[6] that "... in clusters and condensed systems, where electrostatic interactions predominante, CN^- may similarly behave as a spherical core ion". It may also be concluded from the potential rms parameter ΔV that OH^-, ClO_3^-, and BrO_3^- (of the species studied) are likely candidates for exhibiting anisotropies in electrostatic interactions.

The minima $V_<$ of these species are expected to show, barring solvent effects, etc., trends parallel to the respective base strengths and nucleophilicities.[15] Good nucleophiles are expected, in general, to be good bases, viz. good electron donors. Thus, among the species studied, as per the $V_<$ values, OH^- is a "good" nucleophile and ClO_4^- is a relatively "bad" nucleophile. In fact, the trend in $V_<$ values, tabulated in Table I, is in overall agreement with the average nucleophilicity of the anions.[15] For example, CN^- and OH^- show an average nucleophilicity of more than 1000, NO_3^- has a value of 1, and ClO_4^- is assigned a value less than 1. It may be reemphasized here that the correlation of nucleophilicity with $V_<$ in the present study, is approximate in that it does not take into consideration the solvent and experimental effects, such as temperature, concentration, etc.

MESP maps also provide us with a handle on anionic softness parameters.[16] The anionic softness parameter indicates how diffuse, or "fluffy", is the electronic distribution of a given species. This implies that the greater the charge in the negative MESP region, the greater is the corresponding softness parameter (σ). For instance, the σ values for OH^-, SH^-, CN^-, SCN^-, and N_3^- are[16a] 0.0, 0.63, 0.48, 0.84, and 0.78. The respective integrated electron density values (over a region where $V < 0$) are 3.72, 4.13, 4.22, 5.74, and 5.12, thereby revealing similar trends, in general, as shown by the σ parameters above.

In summary, the MESP maps of anions thus provide us with a unifying theme for explaining and predicting various chemical properties such as size, shape, nucleophilicity, and softness of molecular anions.

Acknowledgment. Support from the Alexander van Humboldt-Stiftung and the University Grants Commission, New Delhi, in the form of a Research Fellowship to S.R.G. and I.H.S., respectively, is gratefully acknowledged. We thank Professor Reinhart Ahlrichs for his kind interest and allowing use of computational facilities at the University of Karlsruhe.

---

[15] Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 3rd ed.; McGraw Hill: Kogakusha, Japan, 1970; pp 303–309 and 393.

[16] (a) Marcus, Y. *Ion Solvation*; John Wiley: New York, 1985; pp 47. (b) See also a recent study on hardness by: Harbola, M. K.; Parr, R. G.; Lee, C. *J. Chem. Phys.* **1991**, *94*, 6055. (c) Marcus, Y. *Liquid State Chemistry*; John Wiley: New York, 1977.

Contribution from the Department of Chemistry,
La Trobe University, Bundoora, Victoria 3083, Australia

Complexes of Tetrathiomolybdate and -tungstate with Copper(I) and Silver(I): Sulfur-33 NMR Properties

M. Kony, R. T. C. Brownlee,* and A. G. Wedd*

Received October 2, 1991

Introduction

Sulfur has a vast chemistry, but direct spectroscopic probes are conspicuously lacking. ^{33}S NMR is an obvious possibility, but the isotope has a low natural abundance (0.76 atom %), a small gyromagnetic ratio, and a significant electric quadrupole moment.[1] Consequently, ^{33}S NMR is relatively insensitive and line widths can be broad. However, careful choice of both compounds and appropriate experimental methods can provide information of structural significance.[2-4]

---

(1) (a) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983. (b) For these relatively small molecules with short rotational correlation times, the extreme narrowing regime is expected to apply. See, for example: Butler, A.; Eckert, H. *J. Am. Chem. Soc.* **1989**, *111*, 2802.

(2) Farrar, T. C.; Trost, B. M.; Tang, S. L.; Springer-Wilson, S. E. *J. Am. Chem. Soc.* **1985**, *107*, 262.

(3) Belton, P. S.; Cox, I. J.; Harris, R. K. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 63.

(4) Eckert, H.; Yesinowski, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 2140.

0020-1669/92/1331-2281$03.00/0

Table I. ^{33}S NMR Data[a]

compd	solvent	δ, ppm[b]	ω, Hz
$(Et_4N)_2[MoS_4]$	MeCN	373	45
$(NH_4)_2[MoS_4]$	H_2O	344	38
$(Pr^n{}_4N)_2[(CN)CuS_2MoS_2]$	MeCN	445	257
$(Pr^n{}_4N)_2[(PhS)CuS_2MoS_2]$	MeCN	436	383
$(Pr^n{}_4N)_2[(CN)AgS_2MoS_2]$	MeCN	257	830
$(Pr^n{}_4N)_2[(CN)CuS_2MoS_2Cu(CN)]$	MeCN	139	835
$(Et_4N)_2[WS_4]$	MeCN	183	24
$(NH_4)_2[WS_4]$	H_2O	159	13
$(Pr^n{}_4N)_2[(CN)CuS_2WS_2]$	MeCN	248	404
$(Pr^n{}_4N)_2[(CN)AgS_2WS_2]$	MeCN	106	974
$(Pr^n{}_4N)_2[(CN)CuS_2WS_2Cu(CN)]$	MeCN	16	959

[a] 40 °C; spectrometer frequency, 15.3 MHz; concentrations were 0.4 M except for that of $(Et_4N)_2[MS_4]$ in MeCN, which was 0.1 M. [b] Referenced to 2 M aqueous Cs_2SO_4.

For fast isotropic molecular rotation,[1b] the line width at half-height, ω, is related to the asymmetry parameter, η, the quadrupole moment, eQ, the electric field gradient at the ^{33}S nucleus, eq, and the molecular correlation time, τ, by[1]

$$\pi\omega = 0.1(1 + \eta^2/3)(eQ)^2(eq)^2\tau \qquad (1)$$

Observed line widths are very sensitive to the factors eq and τ.

Line widths of four-coordinate sulfur species (sulfones, sulfonic acid derivatives) are much narrower than those of two- and three-coordinate analogues (sulfides, sulfoxides, etc.), apparently a function of field gradient.[2,3] In addition, terminal thio ligands in the simple thiomolybdates and -tungstates $[MO_{4-n}S_n]^{2-}$ (M = Mo, W; n = 1–4) exhibit fairly narrow line widths in the range 10–400 Hz.[5,6] This property appears to be a function of M–S π bonding reducing the effective p-electron density at the sulfur nucleus with a consequent reduction in field gradient.[6,7]

The thiometallates act as bidentate ligands to a range of metal atom centers.[8] Work from this laboratory has documented a linear correlation between ^{95}Mo and ^{183}W chemical shifts for the thiometalates $[MO_{4-n}S_n]^{2-}$,[9] and this correlation has been extended[6,10] to ^{33}S and ^{17}O chemical shifts. ^{95}Mo and ^{183}W spectra have been reported[9] for the bi- and trinuclear complexes $[(CN)M'S_2MS_2]^{2-}$ (M′ = Cu, Ag) and $[(CN)CuS_2MS_2Cu(CN)]^{2-}$, and the present paper details a ^{33}S NMR study of these species.

Experimental Section

The cyano compounds were synthesized and characterized according to ref 9, and the thiolato analogues via ref 11. MeCN was dried with P_2O_5 prior to fractional distillation.

The ^{33}S spectra were measured at 40 °C on solutions of concentration 0.1–0.4 M prepared in dried degassed MeCN or degassed deionized H_2O and sealed into glass sample tubes. Spectra were acquired with a JEOL FX-200 spectrometer operating at a resonance frequency of 15.3 MHz using a specially constructed horizontal solenoid coil[12] tuned to ^{33}S. The 90° pulse width was typically 23 μs. The spectra were acquired using a modified ACOUSTIC[13] sequence in order to minimize acoustic ringing effects and to reduce the dead time required. The number of transients required to obtain a good signal to noise ratio varied with concentration and line width and was in the range 10^4–10^6 (0.5–6 h accumulation time) in the present work.

The spectra were obtained without using a lock, and the chemical shifts are quoted relative to external 2 M cesium sulfate.[14] Chemical shifts for compounds with narrow (<400 Hz) and broad (>400 Hz) line widths are considered to be accurate to 4 and 8 ppm, respectively (Table I). See ref 14 for comments on the concentration dependence of ^{33}S chemical shifts.

Results and Discussion

Observed chemical shifts, line widths, and structural assignments are given in Table I. Our experimental capabilities permit observation of resonances with line widths less than 3000 Hz. Up to 10^6 transients were required at 40 °C to achieve satisfactory signal to noise ratios (>3) in the concentration ranges available (0.1–0.4 M).

As a result of the high point symmetry (T_d) and consequent low field gradient at sulfur, a single narrow resonance is observed for $[MS_4]^{2-}$ (M = Mo, W) (Table I) and can be assigned unequivocally to a terminal sulfur atom.[5,6]

Line widths increase by at least an order of magnitude upon binding of $[MS_4]^{2-}$ to M′(CN). *One* signal only was seen for all the binuclear and trinuclear anions examined (Table I). The known static structures[9,11] feature a single sulfur site in $[(CN)CuS_2MS_2Cu(CN)]^{2-}$ and, respectively, two and three inequivalent sulfur sites in $[(CN)M'S_2MS_2]^{2-}$ and $[(PhS)CuS_2MS_2]^{2-}$. It is possible that some of the individual resonances are too broad to be observed with the present experimental capabilities, and this would apply particularly to the PhSCu site in $[(PhS)CuS_2MoS_2]^{2-}$.[2,3]

However, it is also likely that rapid ligand exchange leads to a single exchange-averaged signal for the thio ligand sites. Substitution of Ag^I for Cu^I in both the Mo and W binuclear complexes results in a significant increase in line width. Intriguingly, the ^{95}Mo line widths showed the opposite behavior.[9] The observations cannot be rationalized by differences in molecular correlation time. It is probable that exchange effects are influencing the observations.

The $[MS_4]^{2-}$ units are acting as bidentate dithiolate ligands in the present systems. Rapid exchange is a characteristic of dithiolate ligands, especially when bound to d^{10} Cu^I or Ag^I centers.[15] Unfortunately, variable-temperature studies could not be used to probe possible exchange effects as the ^{33}S resonances will be broadened at lower temperatures by the longer molecular correlation times.

Acknowledgment. The Australian Research Council is thanked for financial support. We thank a reviewer for pertinent suggestions.

Registry No. $[(CN)CuS_2MoS_2]^{2-}$, 80011-36-5; $[(CN)AgS_2MoS_2]^{2-}$, 86430-75-3; $[(CN)CuS_2WS_2]^{2-}$, 90790-28-6; $[(CN)AgS_2WS_2]^{2-}$, 86430-77-5; $[(CN)CuS_2MoS_2Cu(CN)]^{2-}$, 80642-82-6; $[(CN)CuS_2WS_2Cu(CN)]^{2-}$, 90790-32-2.

---

(5) Kroneck, P.; Lutz, O.; Nolle, A. *Z. Naturforsch.* **1980**, *35A*, 226.

(6) Belton, P. S.; Cox, I. J.; Harris, R. K.; O'Connor, M. J. *Aust. J. Chem.* **1986**, *39*, 943.

(7) Townes, C. H.; Dailey, B. P. *J. Chem. Phys.* **1949**, *17*, 782.

(8) Muller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(9) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519.

(10) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831.

(11) Acott, S. R.; Garner, C. D.; Nicholson, J. R.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 713.

(12) Shehan, B. P.; Kony, M.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *J. Magn. Reson.* **1985**, *63*, 343.

(13) Patt, S. L. *J. Magn. Reson.* **1982**, *49*, 161.

(14) Belton, P. S.; Cox, I. J.; Harris, R. K. *Magn. Reson. Chem.* **1986**, *24*, 171.

(15) For example: Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M.; Fraser, A. J. F. *Inorg. Chem.* **1982**, *21*, 2397.

Contribution from the Department of Chemistry,
Moorhead State University, Moorhead, Minnesota 56563

Newly Resolved ESR Spectrum of a Low-Spin Cobalt(II) Macrocyclic Complex in 3-Methylpyridine

Abbas Pezeshk

Received December 10, 1991

Introduction

We have previously reported the electron spin resonance (ESR) studies of 1:1 adducts of low-spin cobalt(II) dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenate, CoL.[1] In an attempt