TABLE I

INFRARED SPECTRA OF THE OSMIUM COMPLEXES IN THE CARBONYL STRETCHING REGION[a]

$f_4fosOs_3(CO)_{11}$	2088 (10)	2063 (8)	2040 (1)	2020 (10)	2010 (10)	2006 (8) sh	1993 (8)	1982 (5)	1952 (6)
$f_4fosOs_3(CO)_{10}$	2097 (6)	2033 (4) sh	2023 (8)	2010 (10)	1984 (5)	1970 (4)	1960 (4)	1950 (1)	
$f_4fosOs_2(CO)_6$	2082 (9)	2050 (10)	2016 (8)	1992 (4)	1978 (8)	1972 (5)			
$(f_4fos)_2Os_3(CO)_8$[b]	2064 (2)	2008 (7)	2002 (6) sh	1982 (10)	1950 (4)	1932 (2)			
$f_8fosOs_3(CO)_{11}$	2100 (7)	2088 (5)	2048 (10)	2034 (8)	2025 (8)	2016 (4)	2009 (8)	1989 (6)	

[a] Run on a Perkin-Elmer 457 spectrometer in cyclohexane solution. Relative intensities are given in parentheses. [b] Run in dichloromethane.

ogous ruthenium complexes.[6] One of these, $ffarsRu_3(CO)_{10}$, has been shown by means of X-ray diffraction[7] to contain a triangle of metal atoms with the equatorial ligand bridging two of these atoms. The infrared spectra in the carbonyl stretching region of the new complexes are shown in Table I. It must be pointed out that there is much greater correlation between the infrared spectra of analogous complexes of ruthenium and osmium with the ligands used in this study than there is between different phosphine–ligand complexes of osmium carbonyl.[2]

Reaction of a 2:1 f₄fos:triosmium dodecacarbonyl mole ratio in refluxing xylene gives a small amount of a white solid, which has six sharp bands in the carbonyl stretching region of its infrared spectrum and has an elemental analysis corresponding to $f_4fosOs_2(CO)_6$. This complex we have assigned the structure shown in Figure 1B by analogy with the complexes $ffarsM_2(CO)_6$[5,6,8] (M = Fe, Ru) whose structures are well established. This type of complex $f_4fosM_2(CO)_6$ is the only one that can be isolated where M = Fe, Ru, and Os. Other complexes such as $f_4fosFe(CO)_3$ do not have ruthenium or osmium analogs, whereas $f_4fosOs_3(CO)_{10}$ does not have an iron counterpart. The complex $f_4fosM_2(CO)_6$ is particularly stable for the elements Fe, Ru, and Os, perhaps because it involves chelation and coordination of the double bond which might stabilize the iron complex, as well as a metal–metal bond which is particularly favored by osmium.

A dark red solid can also be obtained from the reaction of excess ligand with triosmium dodecacarbonyl in xylene; this solid has a carbonyl infrared spectrum closely resembling those of $(ffars)_2Ru_3(CO)_8$ and $(f_4fos)_2Ru_3(CO)_8$.[6] The structure of $(ffars)_2Ru_3(CO)_8$ is known[9] to consist of a ruthenium triangle bridged by two ffars ligands and we have assigned $(f_4fos)_2Os_3(CO)_8$ an analogous structure, as shown in Figure 1C. In this case as in $f_4fosOs_3(CO)_{10}$ (Figure 1A) the ligands have displaced equatorial carbonyl groups, so the four phosphorus atoms would be expected to lie near the plane of the triangle of osmium atoms.

Triosmium dodecacarbonyl and f₈fos react in xylene to give a very small amount of a yellow complex which is probably $f_8fosOs_3(CO)_{11}$. Here the phosphine is coordinated by one phosphorus atom only.

The mass spectra of all these new complexes showed no peaks at an m/e value expected for a parent ion; instead peaks with highest m/e corresponded to $Os_3(CO)_x^{n+}$ where x = 0–12 and n = 1 and 2. Under conditions employed (210°) to volatilize the samples in the mass spectrometer, rearrangement of the complexes must occur to give volatile triosmium dodecacarbonyl and other nonvolatile decomposition products.

Acknowledgments.—We thank the National Research Council of Canada for financial assistance and Dr. M. Green for assistance in preparing the triosmium dodecacarbonyl.

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(7) P. J. Roberts and J. Trotter, in preparation.

(8) F. W. B. Einstein and J. Trotter, *J. Chem. Soc. A*, 824 (1967).

(9) P. J. Roberts and J. Trotter, *ibid.*, *A*, 3246 (1970).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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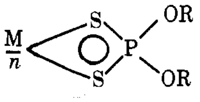
Complexes with Sulfur and Selenium Donors. VI. Electron Spin Resonance Spectra of Bis(*O*,*O'*-dialkyldithiophosphato)oxovanadium(IV) and -copper(II) Chelates[1,2]

BY JOHN R. WASSON

Received September 28, 1970

Since 1965 a number of papers[3-9] have appeared describing the electron spin resonance (esr) spectra of transition metal-*O*,*O'*-dialkyldithiophosphate complexes



I

where n is the oxidation state of metal M and R is the alkyl group. A particularly unusual feature in the esr spectra of many of the complexes is the appreciable phosphorus-31 superhyperfine splitting which arises from metal–phosphorus interactions over distances of about 3 Å or longer. The present work was undertaken to confirm what initially appeared to be anomalously large ^{31}P superhyperfine splitting and to inquire into the mechanism(s) of the transferred superhyperfine interaction.

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(1) Part V: J. R. Angus and J. R. Wasson, submitted for publication.

(2) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

(3) N. S. Garif'yanov and B. M. Kozyrev, *J. Struct. Chem. (USSR)*, **6**, 734 (1965); N. S. Garif'yanov, B. M. Kozyrev, and I. F. Gainullin, *ibid.*, **9**, 451 (1968).

(4) S. Gregorio, J. Weber, and R. Lacroix, *Helv. Phys. Acta*, **38**, 172 (1965); N. S. Garif'yanov, B. M. Kozyrev, and S. Z. Luchkina, *J. Struct. Chem. (USSR)*, **9**, 901 (1968).

(5) L. A. Dalton, L. R. Dalton, and C. H. Brubaker, Jr., "Progress in Coordination Chemistry," M. Cais, Ed., American Elsevier, New York, N. Y., 1968, p 526.

(6) J. R. Wasson, S. J. Wasson, and G. M. Woltermann, *Inorg. Chem.*, **9**, 1576 (1970).

(7) D. Shopov and N. D. Yordanov, *ibid.*, **9**, 1943 (1970).

(8) P. M. Solojeikin, N. U. Kopitzia, and N. P. Loseva, *Teor. Eksp. Khim.*, **4**, 708 (1968); G. M. Larin, P. M. Solozhenkin, and N. I. Kopitsya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 426 (1969); N. S. Garif'yanov, S. E. Kamenev, B. M. Kozyrev, and I. V. Ovchinnikov, *Dokl. Phys. Chem.*, **177**, 850 (1967).

(9) M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968).

Experimental Section

The *O,O'*-dialkyldithiophosphoric acids employed in this study were prepared by the alcoholysis of phosphorus(V) sulfide.[10] Solutions of the copper(II) complexes were prepared by adding the dithiophosphoric acid to an ammoniacal solution of copper(II) sulfate (about 0.1 *M*) and extracting the complex into anisole. The esr signals of the copper(II) solutions in anisole disappeared within 2 hr. Attempts to prepare solid copper(II) compounds or to dope crystals of the corresponding diamagnetic bis(*O,O'*-dialkyldithiophosphato)nickel(II) complexes were without success. Presumably, dithiophosphate species are acting as reducing agents to provide diamagnetic copper(I) complexes. The acid HS_2PF_2 is known to form only the Cu(I) complex upon reaction[11] with copper(II) chloride. Solutions of the oxovanadium(IV) complexes in benzene were prepared by adding excess dithiophosphoric acid to a saturated aqueous solution of vanadyl(IV) sulfate (to which a small amount of sodium hydroxide had been addded) and extracting into benzene. The blue solutions obtained in this manner can be refluxed to give tris(*O,O'*-dialkyldithiophosphato)vanadium(III) compounds.[12] Diphenyldithiophosphinic acid, obtained from Aldrich Chemical Co., Milwaukee, Wis., was used to prepare the copper(II) diphenyldithiophosphinate complex by the method described above.

Esr spectra were obtained with a Varian X-band instrument and magnetic field and frequency calibration accessories described previously.[13] Solution spectra were taken at room temperature using a quartz solution cell and a Varian E-4531/V-4531 multipurpose cavity. Cylindrical quartz sample tubes were employed for the frozen solution samples.

Results and Discussion

Typical solution spectra for the oxovanadium(IV) and copper(II) complexes are shown in Figures 1 and 2.

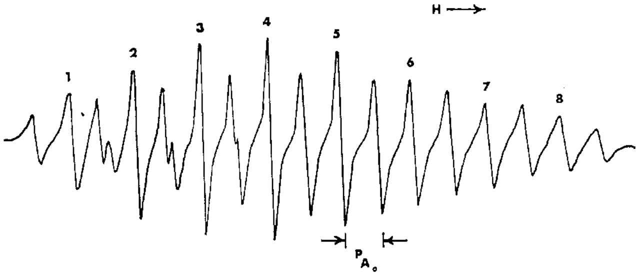

Figure 1.—Esr spectrum of bis(*O,O'*-diethyldithiophosphato)-oxovanadium(IV) in benzene. The eight vanadium hyperfine lines are indicated.

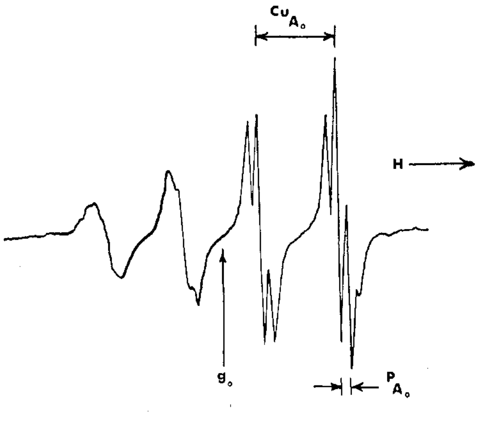

Figure 2.—Esr spectrum of bis(*O,O'*-diethyldithiophosphato)-copper(II) in anisole.

The spectra are consistent with a bis-chelate formulation for the complexes. For both the oxovanadium(IV) and copper(II) complexes the high-field lines are the best resolved.[14] The metal nuclear hyperfine lines are further split into three components with intensity 1:2:1. The magnitude of the ^{31}P superhyperfine splitting in the esr spectra of the oxovanadium(IV) complexes led to line overlapping and fewer than the 24 expected lines were observed. The copper(II) spectra exhibited an additional splitting of the high-field, *i.e.*, $m_I = -{}^3/_2$, line due to superposition of ^{63}Cu and ^{63}Cu isotope lines. Such resolution of ^{63}Cu and ^{65}Cu nuclear hyperfine splitting is not at all uncommon in copper(II)–sulfur donor complexes.[3,7,8,15] The spectra of the oxovanadium(IV) complexes do not indicate the presence of dimeric vanadyl(IV) or vanadium(III) species. Dimeric complexes would be expected to exhibit characteristic spectra[16] and large zero-field splittings[17] mitigate against the detection of vanadium(III) species.

The analysis of the esr spectra of oxovanadium(IV) and copper(II) complexes in solution and in polycrystalline form has been discussed in detail elsewhere.[3,8,15,18] The solution spectra are described by the spin Hamiltonian

$$\hat{H} = g_0\beta H\hat{S} + {}^{M}A_0\hat{S}^{M}\hat{I} + {}^{31P}A_0\hat{S}^{31P}\hat{I}$$

where g_0 is the isotropic g value, β is the Bohr magneton, H is the applied magnetic field, and $^{M}A_0$ and $^{31P}A_0$ are the metal and phosphorus hyperfine splitting constants, respectively. $\hat{S}$ is the spin operator and $^{M}\hat{I}$ and $^{31P}\hat{I}$ are the nuclear spin operators. The spectra of frozen solutions of the dithiophosphate complexes are accounted for using the axially symmetric spin Hamiltonian

$$H = g_{\|}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) + {}^{M}A^{M}I_z\hat{S}_z + {}^{M}B({}^{M}\hat{I}_x\hat{S}_x + {}^{M}\hat{I}_y\hat{S}_y) + {}^{31P}A({}^{31P}\hat{I}_x\hat{S}_x + {}^{31P}\hat{I}_y\hat{S}_y + {}^{31P}\hat{I}_z\hat{S}_z)$$

where $g_{\|}$ and $g_{\perp}$ are the axial g values and the other quantities have their usual significance. The hyperfine splitting constants (in cm^{-1}) are calculated using the expression

$$A = g\beta'(\Delta H) = 4.6688 \times 10^{-5}g(\Delta H)\ \text{cm}^{-1}$$

where g is the appropriate g value, β' is the Bohr magneton in reciprocal centimeters per gauss, and ΔH is the hyperfine splitting measured in gauss. Typical anisotropic esr parameters for oxovanadium(IV) dithiophosphates are $g_{\|} = 1.971$, $g_{\perp} = 1.991$, ${}^{V}A_{\|} = 149 \times 10^{-4}$ cm^{-1}, ${}^{P}A_{\|} = 49 \times 10^{-4}$ cm^{-1}, ${}^{V}A_{\perp} = 48 \times 10^{-4}$ cm^{-1}, and ${}^{P}A_{\perp} = 62 \times 10^{-4}$ cm^{-1}; for copper(II) the values are $g_{\|} = 2.080$, $g_{\perp} = 2.021$, ${}^{Cu}A_{\|} = 158 \times 10^{-4}$ cm^{-1}, ${}^{P}A_{\|} = 11 \times 10^{-4}$ cm^{-1}, ${}^{Cu}A_{\perp} = 39 \times 10^{-4}$ cm^{-1}, and ${}^{P}A_{\perp} = 10 \times 10^{-4}$ cm^{-1}. The anisotropic parameters as well as the isotropic hyperfine constants and g values

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[10] T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Amer. Chem. Soc.*, **67**, 1662 (1945); D. E. Goldberg, W. C. Fernelius, and M. Shamma, *Inorg. Syn.*, **6**, 142 (1960).

[11] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).

[12] C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, *Chem. Commun.*, 1046 (1969).

[13] J. R. Wasson, C. I. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

[14] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957); R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 4445 (1966).

[15] R. Pettersson and T. Vanngard, *Ark. Kemi*, **17**, 249 (1960); J. F. Gibson, *Trans. Faraday Soc.*, **60**, 2105 (1964); T. R. Reddy and R. Srinivasan, *J. Chem. Phys.*, **43**, 1404 (1965); V. F. Anufrienko, E. K. Mamaeva, E. G. Rukhadze, and I. G. Il'ina, *Theor. Exp. Chem. (USSR)*, **3**, 204 (1967); V. F. Anufrienko, T. M. Kogan, E. G. Rukhadze, V. V. Dunina, and E. V. Drobyshevskaya, *ibid.*, **3**, 208 (1967); P. M. Solozhenkin and N. I. Kopitsya, *J. Struct. Chem. (USSR)*, **8**, 470 (1967); L. J. Theriot, K. K. Ganguli, S. Kavarnos, and I. Bernal, *J. Inorg. Nucl. Chem.*, **31**, 3133 (1969).

[16] R. L. Belford, N. D. Chasteen, H. So, and R. E. Tapscott, *J. Amer. Chem. Soc.*, **91**, 4675 (1969).

[17] G. M. Zverev and A. M. Prokorov, *Sov. Phys. JETP*, **7**, 707 (1958).

[18] H. A. Kuska, Ph.D. Thesis, Michigan State University, 1965.

TABLE I

ISOTROPIC ESR PARAMETERS FOR OXOVANADIUM(IV) COMPLEXES

Alkyl substituent of *O,O′*-dialkyldithiophosphate	g_0	$10^4\,{}^{V}A_0$, cm^{-1}	$10^4\,{}^{P}A_0$, cm^{-1}
Ethyl	1.980	86.7	42.1
	(1.986)[a]	(87.2)	(45.4)
n-Propyl	1.990	85.5	42.0
Isopropyl	1.979	85.7	39.7
n-Butyl	1.981	86.7	42.5
sec-Butyl	1.980	86.9	44.4
Isobutyl	1.979	86.6	42.0
2-Phenylethyl	1.979	83.2	41.4
Di-*n*-propyldithiophosphinate[a]	1.985	88.0	26.0
Diethyldithiocarbamates[b]	1.982	79–86	...
$S_2C_2(CN_2)^{2-}$ [c]	1.984	71	...
$S_2C_6Cl_4^{2-}$ [c]	1.987	68	...
$V(S_2CN(C_2H_5)_2)_4$[d]	1.975	66.9	...

[a] Reference 3. [b] B. J. McCormick, *Inorg. Chem.*, 7, 1965 (1968); B. J. McCormick and E. M. Bellott, Jr., *ibid.*, **9**, 1779 (1970). [c] N. M. Atherton, J. Locke, and J. A. McCleverty, *Chem. Ind.* (*London*), 1300 (1965); J. A. McCleverty, J. Lacke, B. Ratcliff, and E. J. Wharton, *Inorg. Chim. Acta*, **3**, 283 (1969). [d] D. C. Bradley, R. H. Moss, and K. D. Sales, *Chem. Commun.*, 1255 (1969). The complex is presumably eight-coordinate.

TABLE II

ISOTROPIC ESR PARAMETERS FOR COPPER(II) COMPLEXES[a]

Alkyl substituent of *O,O′*-dialkyldithiophosphate	g_0	$10^4\,{}^{Cu}A_0$, cm^{-1}	$10^4\,{}^{P}A_0$, cm^{-1}
Ethyl	2.049	69.4	9.1
	(2.045)[b]	(70.7)	(8.6)
n-Propyl	2.048	69.8	9.8
Isopropyl	2.047	69.8	8.8
n-Butyl	2.048	70.3	9.1
sec-Butyl	2.046	69.3	8.6
Isobutyl	2.047	68.8	9.3
m-Xylene[c]	2.046	71.6	9.1
Diphenyldithiophosphinate	2.053	66.1	5.6
Di-*n*-propyldithiophosphinate[b]	2.054	66.2	5.7
Diethyldithiophosphinate[c]	2.054	67.1	5.1
Diethyldithiocarbamate[d]	2.045	80	...
$S_2C_2(CN)_2^{2-}$ [e]	2.067	80	...

[a] Anisole solution. [b] Reference 3. [c] G. M. Larin, *et al.*[8] [d] Reference 9. [e] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

(Tables I and II) are not significantly affected by variation of the alkyl substituent. This result is in agreement with previous work.[3,7,8] Substituent variation was also found to produce negligible effects on the position and intensity of the electronic absorption bands of tris(*O,O′*-dialkyldithiophosphato)chromium(III) compounds.[6] However, replacement of the alkoxy group in dithiophosphate complexes by alkyl[3,8] groups or the phenyl group results in a slight increase in *g* values of the copper(II) complexes and significant *reductions* in the ^{31}P superhyperfine splitting in both oxovanadium(IV) and copper(II) complexes. For the dithiophosphinate complexes there is again an apparent independence of the esr spectra of substituent. Comparison of X-ray crystallographic data for nickel(II) dithiophosphates[19] and dithiophosphinates[20] shows that the P–S bond is slightly shorter and the S–P–S angle is larger in the dithiophosphates. The O–P–O bond angle (~97°) in dithiophosphates is smaller than the C–P–C angle (~107°) in dithiophosphinates. Since a greater degree of P 3s orbital character can be associated with the shorter P–S bond distance and wider S–P–S bond angle in dithiophosphates, a greater P 3s orbital participation can be attributed to the bonding in dithiophosphate chelate rings and larger ^{31}P superhyperfine splitting in dithiophosphates than in dithiophosphinates is not unreasonable. This interpretation is also consistent with the essential constancy of the ^{31}P splitting constants in the solid state and in solution. If the unpaired electrons were delocalized into phosphorus d orbitals and the ^{31}P hyperfine splitting arose from polarization of inner electrons, *i.e.*, 3s, the anisotropic superhyperfine parameters would be much larger than the isotropic ones. Table I presents isotropic esr parameters for oxovanadium(IV) dithiophosphates and permits comparison with related complexes. In vanadyl complexes with vanadium–sulfur bonds both σ and π bondings are significant as studies[21,22] of the electronic and infrared spectra have demonstrated. However, with regard to esr studies of oxovanadium(IV) species it must be borne in mind that the unpaired electron resides in an essentially nonbonding orbital which is sometimes associated with some weak in-plane π bonding. Esr studies[9,23] of complexes containing copper(II)–sulfur bonds have shown that the compounds possess strongly covalent σ bonds. Table II lists isotropic esr data for copper(II) dithiophosphates and related complexes. The copper nuclear hyperfine splitting constants follow the order: dithiophosphinate > dithiophosphate > dithiocarbamate = $S_2C_2(CN)_2^{2-}$. For oxovanadium(IV) the reverse order is found.

The isotropic ^{31}P superhyperfine splitting can be employed to obtain an estimate of the P 3s contribution to the ground-state orbital of the unpaired electron in the oxovanadium(IV) and copper(II) complexes. The isotropic ^{31}P splitting is given by the familiar expression

$$^{31P}A = \frac{8\pi}{3} g_e g_n \beta_e \beta_n |\psi 3s(0)|^2 c_s^2$$

where c_s is the coefficient of the P 3s orbital in the molecular orbital containing the unpaired electron and $|\psi 3s(0)|^2$ is the 3s electron density at the nucleus. The evaluation of c_s^2 is accomplished[24] by taking the ratio of the observed isotropic ^{31}P superhyperfine splitting, A_{obsd}, to that calculated, A_{calcd}, for an unpaired electron residing in a phosphorus 3s orbital, *i.e.*

$$c_s^2 = A_{\text{obsd}}/A_{\text{calcd}} = \frac{A_{\text{obsd}}}{3640\ \text{gauss}}$$

For the oxovanadium(IV) dithiophosphates c_s^2 was estimated to be 0.0135 and for the copper complexes 0.0026. The vanadyl dithiophosphates possess approximate C_{2v} symmetry. The unpaired electron resides in an $^2A_1$ ground state. It is important to note that the vanadium $d_{z^2-y^2}$ orbital is not strongly σ bonding with respect to sulfur but does possess the correct symmetry to interact *directly* with phosphorus 3s and 3p orbitals. This indicates that the *major* source of the large ^{31}P superhyperfine splitting in vanadyl dithiophos-

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(19) P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, **7**, 2625 (1968); P. E. Jones, G. B. Ansell, and L. Katz, *Acta Crystallogr., Sect. B*, **25**, 1939 (1969).

(20) J. F. McConnell and V. Kastalsky, *ibid.*, **22**, 853 (1967); Q. Fernando and C. D. Green, *J. Inorg. Nucl. Chem.*, **29**, 647 (1967).

(21) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968); B. J. McCormick and E. N. Bellott, Jr., *ibid.*, **9**, 1779 (1970).

(22) N. M. Atherton, J. Locke, and J. A. McCleverty, *Chem. Ind.* (*London*), 1300 (1965); J. A. McCleverty, J. Locke, B. Ratcliff, and E. J. Wharton, *Inorg. Chim. Acta*, **3**, 283 (1969).

(23) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964); K. J. Standley and P. F. Taylor, *Proc. Phys. Soc., London* (*Solid State Phys.*), 55 (1968).

(24) P. W. Atkins and M. C. Symons, "The Structure of Inorganic Radicals," American Elsevier, New York, N. Y., 1967, pp 20–22.

phate complexes can be attributed to a direct metal 3d–phosphorus 3s interaction. Delocalization of the unpaired electron to the phosphorus atom *via* metal–sulfur interaction is also expected to contribute to the observed ^{31}P hyperfine structure. The copper(II) dithiophosphate complexes possess approximate D_{2h} symmetry and the unpaired electron resides in a $^2B_{1g}$ antibonding orbital which can be expressed in a form similar to that for the ground state of the vanadyl complexes. In contrast to the vanadyl complexes the copper $3d_{xy}$ orbital is strongly σ bonding to the sulfur atoms but is π bonding with respect to the phosphorus 3s orbitals (*i.e.*, noninteracting since the overlap integrals vanish by symmetry). Thus, the *major* source of ^{31}P superhyperfine splitting in the esr spectra of the copper(II) complexes arises from electron delocalization *via* sulfur to the phosphorus atoms.

Summary

The preceding paragraphs have considered the esr spectra of vanadyl(IV) and copper(II) *O,O'*-dialkyldithiophosphates and related compounds. The reported data are in good agreement with previous work and support ideas concerning the strong covalency of metal–sulfur bonds. The ^{31}P superhyperfine structure in the esr spectra is interpretable in terms of a direct V(3d)–P(3s) interaction in the vanadyl complexes and by delocalization involving the sulfur atoms in the case of the copper(II) complexes. It is unfortunate that both the vanadyl and copper dithiophosphates are unstable since single-crystal studies of the complexes would be most helpful for a detailed elucidation of the electronic structures of the complexes. The instability of the copper complexes with respect to Cu(I), also noted by other investigators,[25] casts some doubt on the interpretation of the electronic spectra reported by Shopov and Yordanov.[7] However, their conclusion of strong metal–sulfur in covalency is not expected to be significantly affected.

Acknowledgments.—The author is grateful to Dr. Charles Trapp, University of Louisville, for his support and encouragement of the initial studies on dithiophosphate complexes and to Dr. B. Jack McCormick, University of West Virginia, for esr data on oxovanadium(IV) dithiocarbamate complexes prior to publication. The author also wishes to thank the University of Kentucky Research Foundation for partial support of this work.

[25] R. A. Palmer, Duke University, personal communication.

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Characterization of a New Class of Diamagnetic Copper(II) Species

BY S. GUPTA, K. C. KALIA, AND A. CHAKRAVORTY*

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Numerous examples of di- and multinuclear systems in which two or more copper(II) atoms undergo antiferromagnetic interactions are known.[1-3] However, discrete and stable molecular species containing two copper(II) atoms and having a *sole population of a singlet ground state* in both the solid and solution phases are rare. The best known example[4] is probably the complex $Cu_2(dpt)_4$, derived from 1,3-diphenyltriazene, $C_6H_5NHN{=}NC_6H_5$ (abbreviated as Hdpt). In this report a new class of neutral, dinuclear, and diamagnetic copper(II) chelates, $Cu_2(aao)_4$, derived from arylazooximes,[5] $ArN{=}NC(R){=}NOH$ (abbreviated as Haao), is described.

Experimental Section

Preparation of Compounds.—The **arylazooximes** were synthesized according to methods described elsewhere.[5] The **copper(II) complexes** were prepared by adding a methanolic solution of the ligand (0.02 mol) to a methanolic solution of copper(II) acetate monohydrate (0.01 mol). The dark mixture was digested on the steam bath for 15 min and was then allowed to cool. The crystals were collected and then recrystallized from chloroform–ethanol or chloroform–hexane mixture. The shining dark brown to black crystals were obtained in 60–70% yields.

β-(α-Oximinoethyl)phenylhydrazine, $C_6H_5NHNHC(CH_3){=}NOH$, **1**, was prepared by hydrogenating (50 psi, 4 hr, 24°) ω-nitroacetaldehyde phenylhydrazone[6] (2 g) in 95% ethanolic solution (50 ml) in the presence of palladium–charcoal catalyst (10%, 0.1 g). At the end of hydrogenation, the reaction mixture was warmed to dissolve the white crystalline solid that had separated. The solution was quickly filtered from the catalyst and was then cooled in the refrigerator. The shining needles were recrystallized from ethanol (yield 60%). The melting point of the pure compound was 122°. *Anal.* Calcd for $C_8H_{11}N_3O$: C, 58.20; H, 6.67; N, 25.45. Found: C, 58.50; H, 6.90; N, 25.75. The reduction of ω-nitroacetaldehyde phenylhydrazone to **1** with ammonium sulfide was described by Bamberger.[7] However, we found the above catalytic reduction procedure to be a very convenient one.

Oxidation of 1 in the Presence of Metal Ions.—(i) When solutions of **1** (0.03 mol) and cobalt(II) acetate tetrahydrate (0.01 mol) were mixed in the absence of oxygen (*i.e.*, under vacuum or in nitrogen atmosphere), no marked change was visible. However as soon as air was introduced, the solution turned deep purple and crystals of **tris(phenylazoacetaldoximato)cobalt(III)**[8] started depositing within a few minutes. The same product was obtained when **1** was warmed with $[Co(NH_3)_6]Cl_3$ in aqueous methanol.

(ii) When a methanolic solution of **1** (0.01 mol) was treated with aqueous K_2PdCl_4 (0.01 mol) in the presence of air, **di-μ-chloro-bis(phenylazoacetaldoximato)dipalladium(II)**[9] was obtained in good yield.

(iii) Similarly the reaction (in air) of **1** (0.02 mol) with copper(II) acetate monohydrate (0.01 mol) in methanolic solution produced an instantaneous brown color. Shining dark brown crystals started separating from the solution in a few minutes (yield 70%). This compound was identical in all respects to the compound obtained by treating (*vide supra*) copper(II) acetate monohydrate with phenylazoacetaldoxime.

Measurements.—**Pmr spectra** were determined on a Varian HR 100 spectrometer. A Cary 14 recording spectrophotometer and a Perkin-Elmer 521 recording spectrophotometer were used to study **electronic** and **vibrational spectra**, respectively. The **molecular weight** of one complex was determined in carefully purified benzene using the cryoscopic procedure in the presence of sodium sulfate.[10] The **magnetic nature** of the compounds was

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[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[2] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969).

[3] R. L. Martin, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968, p 175.

[4] C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959); C. Furlani and F. DiTella, *Gazz. Chim. Ital.*, **90**, 280 (1960).

[5] K. C. Kalia and A. Chakravorty, *J. Org. Chem.*, **35**, 2231 (1970).

[6] E. C. S. Jones and J. Kenner, *J. Chem. Soc.*, 919 (1930).

[7] E. Bamberger and J. Frei, *Ber.*, **35**, 1084 (1932).

[8] K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, **7**, 2016 (1968).

[9] K. C. Kalia and A. Chakravorty, *ibid.*, **8**, 2586 (1969).

[10] H. M. Roberts and C. R. Bury, *J. Chem. Soc.*, **123**, 2037 (1923).