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.

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

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Received October 21, 1970

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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TABLE I

CHARACTERIZATION OF COMPOUNDS

R	Ar	Empirical formula	Mp,[a] °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Cu[b] Calcd	% Cu[b] Found
CH_3	C_6H_5	$C_{16}H_{16}N_6O_2Cu$	168–169 dec	49.55	49.41	4.13	4.36	21.68	21.38	16.40	16.14
n-C_3H_7	C_6H_5	$C_{20}H_{24}N_6O_2Cu$	150	54.12	54.23	5.41	5.53	18.94	18.82	14.32	13.79
C_6H_5	C_6H_5	$C_{26}H_{20}N_6O_2Cu$	174–175	61.00	60.45	3.91	4.25	16.43	16.32	12.42	12.25
p-$C_6H_4CH_3$	C_6H_5	$C_{28}H_{24}N_6O_2Cu$	181	62.27	61.91	4.45	4.74	15.57	15.78	11.77	11.96

[a] All melting points reported in this table are uncorrected. [b] Copper was estimated gravimetrically as copper(I) thiocyanate after decomposing the complex with a mixture of nitric and hydrochloric acids.

determined using a sensitive Gouy balance described elsewhere.[11]

Results and Discussion

The copper(II) complexes, reported for the first time, were synthesized by straightforward chelation reactions between copper(II) acetate and arylazooximes in methanolic solution. The complex obtained by the reaction

$$2C_6H_5N{=}NC(CH_3){=}NOH + Cu^{2+} \longrightarrow$$

is identical with the complex obtained by the reaction

$$2C_6H_5NHNHC(CH_3){=}NOH + Cu^{2+} \xrightarrow{\text{air}}$$

The oximinohydrazine apparently undergoes fast aerial oxidation to the arylazooxime in the presence of copper(II) ion. Similar facile oxidations also occur in the presence of cobalt(II) or -(III) and palladium(II).

Characterization data for the copper(II) complexes are collected in Table I. The empirical formula of the complexes corresponds to $Cu(aao)_2$. They are uniformly diamagnetic in the solid state (27°).

Some properties in the solution phase will be illustrated with the specific example of the complex derived from phenylazobutyraldoxime. Bulk susceptibility measurements in benzene solution showed the complex to be diamagnetic (27°). It exhibits well-resolved pmr bands in chloroform (and benzene) solution. In general the chemical shifts and spin–spin splittings (Table II) are very close to those of the corresponding free ligand[5] and its halogen-bridged palladium(II) chelates.[9] We believe that this is a very convincing demonstration that the concentration of paramagnetic species, if any, is very small. The $CH_3CH_2\mathit{CH_2}$ signal is relatively broad (width at half-height $\Delta\nu_{1/2} \approx 25$ Hz) and the spin–spin splitting is not clearly resolved. It might be argued that this is due to dipolar broadening arising out of a small population of a paramagnetic state. However, it is to be noted that in the halogen-bridged palladium(II) complex also the corresponding signal is broad ($\Delta\nu_{1/2} \approx 20$ Hz) and the triplet spin–spin structure is just visible. The molecular weight of the complex determined cryscopically in benzene was repeatedly found to lie in the range 890 ± 20. This shows that the complex is *dimeric* (calculated mol wt 887).

Due to solubility reasons the molecular weight of the other complexes could not be determined. However, in chloroform solution all the complexes give rise to pmr lines (Table II) which are as sharp ($\Delta\nu_{1/2} \approx 3$–4 Hz) as those of the free ligand. The electronic spectra (Table III) of the complexes are very similar to each other with a prominent feature at ~770 nm. We infer that the complexes, in general, are dimeric and have the molecular formula of the type $Cu_2(aao)_4$.

TABLE II

PROTON RESONANCE FREQUENCIES[a] OF COPPER COMPOUNDS

R	Ar	Group	Chem shift,[b] ppm
CH_3	C_6H_5	CH_3	2.21
n-C_3H_7	C_6H_5	$\mathit{CH_3}CH_2CH_2$	1.02[c]
		$CH_3\mathit{CH_2}CH_2$	1.78[d]
		$CH_3CH_2\mathit{CH_2}$	2.77[e]
p-$C_6H_4CH_3$	C_6H_5	*p*-$C_6H_4\mathit{CH_3}$	2.50

[a] Aromatic protons give signals in the region 6.80–8.25 ppm and are not tabulated. [b] The pattern, the widths, and the chemical shifts of signals are very similar to those of the free ligands. Chemical shifts are from tetramethylsilane measured at 100 MHz in $CDCl_3$. [c] Center of a triplet ($J = 7$ Hz). [d] Center of a sextet ($J = 7$ Hz). [e] Center of a broad signal with width at half-height ~25 Hz.

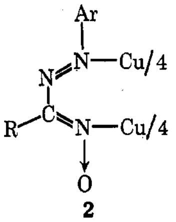
TABLE III

WAVELENGTHS (λ, NM) AND EXTINCTION COEFFICIENTS (ε, L. MOL^{-1} CM^{-1}) OF ELECTRONIC BANDS IN BENZENE

R	Ar	λ (ε)
CH_3	C_6H_5	770 (1700), 580[a] (4400), 447 (13,180)
n-C_3H_7	C_6H_5	780 (2100), 580[a] (4740), 450 (14,100)
C_6H_5	C_6H_5	785 (1700), 483 (12,500)
p-$C_6H_4CH_3$	C_6H_5	785 (2240), 488 (12,440)

[a] Shoulder.

At present we are not in a position to make any definite statements about the structure of the complexes. A $Cu_2(CH_3COO)_4$-like structure[3] ($Cu_2(dpt)_4$ presumably belongs[4] to the same structural type) with bridging arylazooxime units is a distinct possibility. Of the several possible modes of bridging two are **2** and **3**. On the basis of ir data, the presence of the chelate ring **4** was suggested for the arylazooxime complexes of cobalt(III),[8] rhodium(III),[9] and palladium(II).[9] In **2** the sites of linkage to the metal are the same as those in **4**. On the other hand, **3** contains triatomic bridging units like those in $Cu_2(CH_3COO)_4$ and $Cu_2(dpt)_4$. The infrared spectra of the $Cu_2(aao)_4$ complexes were examined but these did not throw much light on the structural problem. A three-dimensional X-ray diffraction work on a $Cu_2(aao)_4$ complex is in progress.



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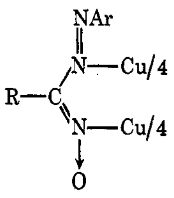

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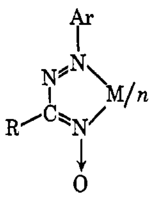

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Acknowledgment.—Thanks are due to Professor M. V. George for making available hydrogenation facilities. The award of a Junior Research Fellowship to S. G. by the CSIR, Delhi, India, is gratefully acknowledged.

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