Preparation and properties of the tetra-μ-acetato-(O,O')-bis(triphenylphosphine)dicopper(II) complex

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On the basis of assumption of the effects which can cause stabilization of oxidation state II in copper complexes with the ligands having strong reduction influence, the reaction of copper(II) acetate with triphenylphosphine (Ph$_3$P) in different solvents was investigated. The complex of stoichiometric composition CuAc$_2$Ph$_3$P was prepared in solvents preferring the existence of dimeric units of copper(II) acetate. The magnetic and spectral properties of the prepared complex indicate that the complex has the structure of dimer in the solid state. The course of the reduction of Cu(II) to Cu(I) was observed under conditions for which the equilibrium in solution is shifted in favour of monomeric copper(II) acetate. These results confirm the rightness of the assumption that the dimeric structure of copper(II) carboxylates may be one of the effects causing the stabilization of oxidation state II in copper complexes.

На основании предположений об эффектах, которые могут обусловить стабилизацию степени окисления II в комплексах меди с лигандами с выраженными восстановительными свойствами были изучены реакции ацетата меди с трифенилфосфином (Ph$_3$P) в различных растворителях. В растворителях, способствующих существованию димерных частиц ацетата меди, был приготовлен комплекс стехиометрического состава Cu-Ac$_2$Ph$_3$P. Магнитные и спектральные свойства полученного комплекса свидетельствуют о том, что в твердом состоянии комплекс имеет структуру димера. В условиях, при которых равновесие в растворе сдвигается в сторону мономера ацетата меди, наблюдался процесс восстановления Cu(II) на Cu(I). Приведенные результаты подтвердили верность предположения, что димерная структура медных карбоксилатов может быть одним из факторов, обуславливающих стабилизацию степени окисления II в комплексах меди.

Triphenylphosphine is one of the ligands L_R (L_R = ligand with strong reduction influence, *e.g.* CN^-, I^-, SCN^-, R_3E, where R = alkyl, aryl and E = P, As, Sb, Bi) the presence of which in the coordination sphere of Cu(II) usually causes a redox decomposition of copper(II) complex. In these reactions the relatively stable complexes of Cu(I) with the ligands L_R in coordination sphere arise. The reducing influence of the ligand Ph_3P is documented by the fact that simple copper(II) salts CuX_2 (X^- = Cl^-, Br^-, NO_3^-, ClO_4^-, BF_4^-, $RCOO^-$, *etc.*) are reduced in its presence [1—6]. Besides the complexes of Cu(I) of stoichiometric composition $[CuX(Ph_3P)_n]$ (n = 1, 2, 3 or 1.5), the formation of triphenylphosphine oxide as final product of oxidation was either proved [4, 5] or assumed [6] in most cases.

On the other hand, the existence of Cu(II) complexes with the ligands L_R in the coordination sphere suggests the possibility to stabilize the oxidation state of Cu(II) by convenient composition of the coordination sphere. The analysis of the data hitherto known from literature about the stabilization of oxidation state II in the presence of ligand L_R in the coordination sphere reveals two effects [7] which may significantly influence this phenomenon:

a) The presence of certain ligands L_S in the coordination sphere of Cu(II) together with ligands L_R.

b) A certain specific structure of the complex with the ligands which do not usually stabilize oxidation state II.

Some triphenylphosphine copper(II) complexes of the composition $Cu(L_S)_2$-(Ph_3P) in which the hexafluoroacetylacetonate [8] or trifluoroacetylacetonate [9] anions function as stabilizing ligands have been prepared up to now. A characteristic example of the stabilizing effect of structure is represented by the complexes $[Cu_4O(X)_6(Ph_3P)_4]$ (X^- = Cl^-, Br^-) [10].

By comparing the data about the reducing influence of Ph_3P on fifteen different carboxylates of Cu(II) [5] with the data about preparation of Cu(II) complexes of the composition $(CH_2 = CH(CH_2)_n COO)_2 \dot{C}uPh_3P$ (n = 1,2) [11] and $((CH_3)_3CCOO)_2CuPh_3P$ [12], we have come to the conclusion [7] that the dimeric structure of Cu(II) carboxylates may cause the stabilization of the oxidation state of Cu(II). This assumption is also supported by the data published in the course of our experiments. These data concern the complex $CuY(Ph_3P)$ [13, 14] (Y = dianion of 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedicarboxylic acid) in which the existence of dimeric structure and Ph_3P—Cu(II) bond was proved by X-ray structural analysis.

Many copper(II) carboxylates in which the reduction of Cu(II) in the presence of Ph_3P was observed [5] also have dimeric structure. In order to contribute to elucidation of the conditions under which the dimeric structure can produce the stabilization of oxidation state in Cu(II) complexes, we aimed at studying the reactions of different copper(II) carboxylates with triphenylphosphine. This paper

deals with the reactions of copper(II) acetate with triphenylphosphine under different conditions.

Experimental

Chemicals

Monohydrate of copper(II) acetate $Cu(CH_3COO)_2 \cdot H_2O$ — anal. grade (Lachema, Brno) was used without any further treatment.

Anhydrous copper(II) acetate $Cu(CH_3COO)_2$ was prepared by thermal dehydration of $Cu(CH_3COO)_2$ H_2O at 120 °C in the presence of phosphorous pentoxide.

Triphenylphosphine $C_{18}H_{15}P$ (Ph_3P) (Lachema, Brno) was purified by three-fold recrystallization from hot ethanol before use.

The solvents (ethanol, methanol, ether, acetone, chloroform, benzene, dioxan) were purified by usual methods [15].

Instruments

The infrared spectra in the region $\bar{v} = 400$—4000 cm^{-1} were measured in nujol suspension on a Specord 75 IR instrument and in KBr pellets on a Perkin—Elmer 180 instrument. The spectra obtained with both instruments exhibited no significant differences. The infrared spectra in the region $\bar{v} = 50$—400 cm^{-1} (FIR) were measured in nujol suspension on a Perkin—Elmer 180 instrument by using a polyethylene cell.

The electronic spectra of solution or nujol suspension in the region $\lambda = 330$—800 nm were measured on a Specord UV VIS instrument. The spectra of nujol suspension in the region $\lambda = 250$—1000 nm were taken on a Beckman UV 5240 instrument.

The magnetic susceptibility was measured at laboratory temperature by the Gouy method with an instrument constructed in the Department of Inorganic Chemistry, Slovak Technical University. The dependence of magnetic susceptibility on temperature in the interval ⟨80 K; 300 K⟩ was measured with Faraday balance. Both instruments were calibrated with $Hg[Co(SCN)_4]$ [16, 17]. The molar magnetic susceptibility of the Cu(II) ions χ_m was corrected [18, 19] for diamagnetism ($\chi_{m,dia} = -288 \times 10^{-11}$ m^3 mol^{-1}) by means of the Pascal constants and for temperature independent paramagnetism ($N_\alpha = 75 \times 10^{-11}$ m^3 mol^{-1}). The effective magnetic moment was calculated from the equation

$$\mu/\mu_B = (3RT \cdot \chi_{m,corr} \cdot \mu_0^{-1} \cdot N_A^{-2} \cdot \mu_B^{-2})^{1/2}$$

The exchange parameter J was calculated using computer ODRA 1204.

The EPR spectra of polycrystalline sample in X-zone were taken at laboratory temperature on a JES-ME-3X instrument.

Analysis

Copper was determined by complexometric titration of aqueous acetonic or aqueous ethanolic solutions of samples (after repeated decomposition with hot concentrated nitric acid diluted with water in the volume ratio 1:1) by using murexide as indicator.

The content of carbon and hydrogen in the samples was determined in the service laboratory of the Department of Analytical Chemistry, Slovak Technical University.

Preparation of $[Cu_2Ac_4(Ph_3P)_2]$

A solution containing Ph_3P (10 mmol; 2.62 g) in dried ethanol (40 cm³) (heated to 40—50 °C for raising the solubility) was added into the solution containing $CuAc_2$ H_2O (5 mmol; 1 g) in dried ethanol (26 cm³) which was cooled with cold water. After 75 min stirring the dark-green microcrystalline product was filtered off and two-times washed with small portions of cooled dried ethanol and subsequently it was dried *in vacuo* in a desiccator over $CaCl_2$. The yield was 1 g.

For $Cu_2Ac_4(Ph_3P)_2$ w_i(calc.): 14.315 % Cu, 59.524 % C, 4.768 % H; w_i(found): 14.10 % Cu, 59.41 % C, 4.80 % H.

Results and discussion

It is known that the monohydrate of copper(II) acetate exists in the solid state in the form of dimer $[Cu_2Ac_4(H_2O)_2]$ [20, 21]. This structure gives rise to exchange interactions of unpaired spins of the atoms of Cu(II) the consequence of which is a subnormal value of the effective magnetic moment [22]. The value of the effective magnetic moment of copper(II) acetate in solution is significantly affected by solvent [23]. According to the increase in these interactions, the solvents were arranged [22] in this order: (water, pyridine); (methanol); (ethanol, acetone, chloroform, benzene); (carbon tetrachloride, dioxan); (ether). This sequence is determined by dielectric properties of the solvent and its coordinating ability [22].

The experiments performed for investigating the course of the reaction of copper(II) acetate with triphenylphosphine in different solvents have shown that only some solvents are suitable for the preparation of the complex of copper(II) acetate with triphenylphosphine. Owing to very low solubility of copper(II) acetate in ether, the beginning of the product formation was observed as late as 24 h after mixing the solutions. The microcrystalline product of the composition $CuAc_2Ph_3P$ was isolated from the system after 60 h stirring. In dioxan which has relatively high coordinating ability with respect to Cu(II), we observed the formation of the complex $CuAc_2 \cdot 0.5$ diox. Because of very low solubility of copper(II) acetate in

benzene and chloroform, these solvents are unsuitable for preparation of the complex in demand. The colour change indicating formation of the complex of copper(II) acetate with triphenylphosphine in acetone appeared immediately after mixing the reactants, but we did not succeed in isolating the product because some redox processes accompanied its formation. The most convenient solvent for the preparation was ethanol in which the formation of the dark-green microcrystalline product of the composition $CuAc_2Ph_3P$ was observed instantaneously after mixing the saturated solutions of reactants at laboratory temperature. The use of dilute solutions or a rise of temperature of the reaction mixture resulted in the fact that a redox process took place in the system. A prolongation of the time of stirring of the saturated solution of reactants brought about that the formed product gradually dissolved and a redox process was also observed. These observations allow to assume that the equilibrium Cu_2Ac_4(dimer)$\rightleftharpoons 2CuAc_2$(monomer) significantly affects character of the isolated products from ethanolic solutions. The optimum conditions under which the product $CuAc_2Ph_3P$ is reproducibly obtained in maximum yield are described in Experimental.

The data characterizing the spectral and magnetic properties of the $CuAc_2Ph_3P$ complex in the solid state are given in Table 1.

The symmetric, asymmetric, and bending vibrations of the carboxyl group appear in the region of wavenumbers typical for the dimeric acetato complexes of Cu(II) [22]. Similarly, the difference between the wavenumbers $\tilde{v}_a - \tilde{v}_s$ suggests the bridging bonding of the carboxyl group.

The positions of band I and II in the electronic spectrum are also in the region typical for copper(II) acetate complexes [25], the only difference being that band I in the spectrum of the $CuAc_2Ph_3P$ complex is at lower energy than in the spectrum of the $CuAc_2H_2O$ complex.

The subnormal value of magnetic moment at laboratory temperature of the $CuAc_2Ph_3P$ complex also indicates an antiferromagnetic superexchange between the Cu^{2+} ions in the dimer. The EPR spectrum of polycrystalline sample at laboratory temperature is typical for the triplet state ($S = 1$) [26]. The qualitative similarity of the spectrum of $CuAc_2Ph_3P$ with spectra of other dimeric Cu(II) carboxylates [27] allows the following assignment of the lines: $B_{\|1} = 57.2$ mT, $B_\perp = 472.1$ mT, and $B_{\|2} = 603.3$ mT. On the basis of this assignment, the parameters of EPR spectrum given in Table 1 were obtained according to [26]. The values thus obtained, especially $g_\|$ are greater than the values for the monohydrate of copper(II) acetate [28] ($g_\perp = 2.073$, $g_\| = 2.344$, $D = 0.345$ cm^{-1}, $E = 0.005$ cm^{-1}). This indicates a greater orbital contribution in the phosphine complex.

The magnetic susceptibility and magnetic moment of $CuAc_2Ph_3P$ (Table 2) show temperature dependence characteristic of antiferromagnetic interactions of two centres coupled in dimer. The value of singlet—triplet separation ($-2J$) was obtained from the modified Bleaney—Bowers equation [26]

Table 1

Data characterizing the spectral and magnetic properties and EPR spectrum of the $CuAc_2Ph_3P$ complex

Infrared spectrum[a]	$\bar{v}/cm^{-1}$
$v_{as}(COO)$	1618 vs
$v_s(COO)$	1414 m
$v_{as} - v_s$	204
$v(X\text{-sens})[b]$	1094 s
$v(OCO)$	680 s
$v_{as}(C—P)[b]$	503 s
$v_s(C—P)[b]$	430 w
$v(Cu—O)$	348 vs
Electronic spectrum[a]	λ_{max}/nm
Band I	717
Band II	375 sh
Charge-transfer bands	276 sh, 266, 211
Magnetic moment[c]	μ_{eff}/μ_B
	1.34
EPR spectrum[d]	
$g_{\parallel}$	2.42
$g_{\perp}$	2.08
g_{av}	2.20
D/cm^{-1}	0.372
E/cm^{-1}	0.0062

a) In nujol suspension.

b) Characteristic vibrations of the Ph_3P ligand; for noncoordinated Ph_3P $v(X\text{-sens})$ $\bar{v} = 1090$ cm^{-1}, $v_{as}(C—P)$ $\bar{v} = 499$ cm^{-1}, and $v_s(C—P)$ $\bar{v} = 420$ cm^{-1} [24].

c) Measured at laboratory temperature by the Gouy method.

d) $g_{av} = \left[\frac{1}{3}\left(2g_{\perp}^2 + g_{\parallel}^2\right)\right]^{1/2}$

$$\chi_{m,corr,Cu} = \frac{N_A \mu_0 g_{av}^2 \mu_B^2}{3kT}\left[1 + \frac{1}{3}\left(e^{E(-2J)/kT}\right)\right]^{-1}(1-x) + \left(\frac{N_A \mu_0 g_{imp}^2 \mu_B^2}{4kT}\right)x$$

where x is mole fraction of the monomeric form of complex and other symbols have usual meaning [29, 30]. The spectroscopic splitting parameter $g_{av} = 2.20$ was obtained from the EPR spectrum. It was used for least-squares method fitting. The quality of fitting was considered from the sum of squared residua

Table 2

Magnetic data[a]

T/K	$\chi_{m,corr,Cu} \cdot 10^{11}/(m^3\ mol^{-1})$	μ_{eff}/μ_B
80	132	0.26
100	204	0.36
120	292	0.47
140	432	0.62
160	522	0.73
180	627	0.85
200	734	0.97
220	807	1.06
240	855	1.14
260	875	1.20
280	907	1.27
295	907	1.31

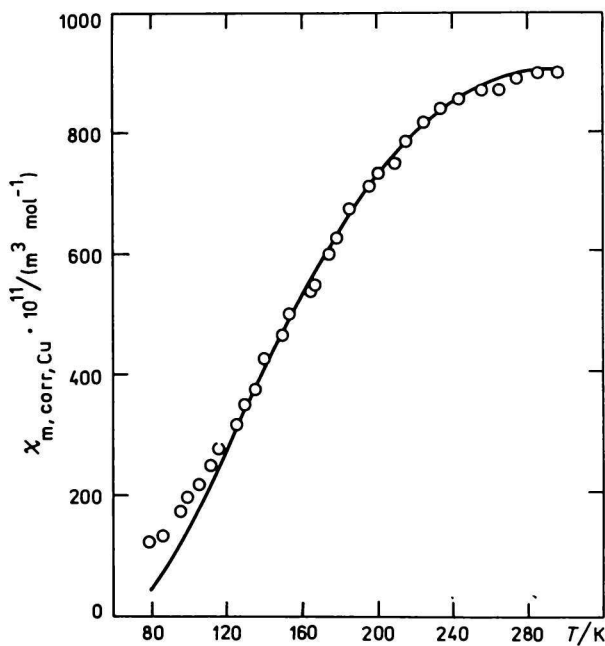*a*) Selected from 48 experimental points.

Fig. 1. Variation of magnetic susceptibility with temperature.
Circles denote experimental data for which the course of plot has been optimized (see the text).

$$ERR = \sum_i (\chi_{m,calc,i} - \chi_{m,exp,i})^2$$

The best agreement of the calculated plot (full line in Fig. 1) with experimental values (circles) was obtained for $J = -175$ cm^{-1} (ERR $= 2.200 \times 10^{-8}$ m^6 mol^{-2}) while the portion of the monomeric form of complex was $x = 0$. The energy of singlet—triplet separation corresponding to $-2J = 350$ cm^{-1} for the CuAc$_2$Ph$_3$P complex is higher than for the acetato copper(II) complexes with other ligands [31]. This fact may be explained by a greater transfer of electron density from Ph$_3$P to the $3d_\sigma$ orbitals owing to a considerable σ-donating ability of the Ph$_3$P ligand.

These data about the properties of the CuAc$_2$Ph$_3$P complex in the solid state enable us to come to the conclusion that the prepared complex in the solid state has the dimeric structure Cu$_2$Ac$_4$(Ph$_3$P)$_2$ in which the atoms of Cu(II) are joined with four bridging acetate groups and the Ph$_3$P ligands occupy the axial positions of dimeric unit Cu$_2$Ac$_4$.

The electronic spectrum (measured 5 min after adding the solvent to the solid sample) of the freshly prepared ethanolic solution of the Cu$_2$Ac$_4$(Ph$_3$P)$_2$ complex ($c_{Cu(II)} = 1.73 \times 10^{-2}$ mol dm^{-3}) exhibits a distinct shoulder at the wavelength of 375 nm ($\varepsilon \approx 88$ mol^{-1} dm^3 cm^{-1}) and a broad absorption band at the wavelength of 710 nm ($\varepsilon \approx 226$ mol^{-1} dm^3 cm^{-1}). The spectrum changes with time, a decrease in absorbance is to be observed in the whole visible region of the spectrum. One hour after the preparation of solution, the decrease in absorbance is about 25 % at the wavelength of 375 nm and about 7 % at the wavelength of 710 nm. The character of the spectrum of Cu$_2$Ac$_4$(Ph$_3$P)$_2$ in solution and the observed changes indicate that the complex decomposes in solution and the existing equilibrium gives rise to the redox process manifesting itself by a decrease of absorbance in the whole region of the spectrum. A more expressive decrease in absorbance at 375 nm is obviously due to the fact that the particles with dimeric grouping of the atoms of Cu(II) absorb radiation in this region, while both dimer and monomer of copper(II) acetate [32] absorb radiation in the region of 700 nm.

The course of thermal decomposition of the Cu$_2$Ac$_4$(Ph$_3$P)$_2$ complex, which is thermally stable up to 130 °C approximately, is interesting in connection with redox process. The thermal decomposition accompanied with a mass loss of ca. 5 % takes place in the temperature interval 135 °C—145 °C. However, the decomposition product is unstable, which results in a small increase in mass (ca. 1 % in the temperature interval 155 °C—170 °C). It is assumed that the total decomposition of the complex proceeds simultaneously with this process or instantaneously after it. Though the results of thermogravimetric investigation may be regarded as preliminary, the mass decrease in the first stage of decomposition may be explained by splitting off the acetate group (theoretical mass loss 6.6 %), which gives rise to a complex containing Cu(I). This explanation is in agreement with the views on the course of a redox process due to the presence of a ligand with

reducing influence in the coordination sphere of Cu(II) [33]. Similarly, the reduction of the $Cu(II)(hfac)_2Ph_3P$ complex in the presence of excess Ph_3P has been explained by origination of a radical from the hexafluoroacetylacetonate ligand (hfac) [8] giving rise to $Cu(I)(hfac)(Ph_3P)_2$.

The presented results (possibility to isolate the $Cu_2Ac_4(Ph_3P)_2$ complex only from certain solvents and properties of this complex in the solid state and solution) confirm the assumption that the dimeric structure is important for the stabilization of oxidation state II in carboxylato complexes of copper.

Note added in proof.

After sending of the manuscript of this paper to the Editor a citation of the paper T. Tokki, T. Ikeda, and Y. Muto, *Bull. Chem. Soc. Jap. 55*, 3925 (1982) appeared in *Chem. Abstr. 98,* 82801 (1983). The authors prepared the green crystals of dimeric copper(II) acetate adduct with triphenylphosphine $Cu(CH_3COO)_2 \cdot Ph_3P$ by reaction of Ph_3P in ether with $Cu(CH_3COO)_2 \cdot H_2O$ in ethanol adding also a few drops of glacial acetic acid. Their results of magnetic susceptibility measurements differ slightly in values of $-2J = 371$ cm^{-1} and magnetic moment $\mu_{eff}/\mu_B = 1.23$ (at 283 K), from those presented in our paper.

References

1. Carty, A. J., Anderson, W. H., Palenik, G. J., and Schreiber, G., *Can J. Chem. 49,* 761 (1971).
2. Cotton, F. A. and Goodgame, D. M. L., *J. Chem. Soc. 1960,* 5267.
3. Jardine, F. H., Rule, L., and Vohra, A. G., *J. Chem. Soc. A1970,* 238.
4. Hammond, B., Jardine, F. H., and Vohra, A. G., *J. Inorg. Nucl. Chem. 33,* 1017 (1971).
5. Reichle, N.˙T., *Inorg. Chim. Acta 5,* 325 (1971).
6. Ondrejovič, G., Makáňová, D., Valigura, D., and Gažo, J., *Z. Chem. 13,* 193 (1973).
7. Ondrejovič, G., Valigura, D., and Koman, M., *Abstract of papers XXII ICCC, Vol. 1,* p. 217. Budapest, 1982.
8. Zelonka, R. A. and Baird, M. C., *Can. J. Chem. 50,* 1269 (1972).
9. Leh, F. and Chan, K. M., *Bull. Chem. Soc. Jap. 45,* 2709 (1972).
10. tom Dieck, H. and Brehm, H. P., *Chem. Ber. 102,* 3577 (1969).
11. Edmonson, B. J. and Lever, A. B. P., *Inorg. Chem. 4,* 1608 (1965).
12. Rakitin, Yu. V., Novotortsev, V. M., Kalinikov, V. T., Pasinskii, A. A., Larin, G. M., Filatov, A. V., and Indrisov, T. Ch., *Koord. Khim. 3,* 807 (1977).
13. Ferguson, G., McAlees, A. J., McCrindle, R., Restivo, R. J., and Roberts, P. J., *J. Amer. Chem. Soc. 99,* 3170 (1977).
14. McCrindle, R., Ferguson, G., McAlees, A. J., and Roberts, P. J., *J. Chem. Soc., Dalton Trans. 1981,* 1406.
15. Organikum, *Organická synthesa.* (Organic Synthesis.) Academia, Prague, 1971.
16. Figgis, B. N. and Nyholm, R. S., *J. Chem. Soc. 1958,* 4190.
17. Rade, H. St., *J. Chem. Phys. 77,* 424 (1973).
18. Earnshaw, A., *Introduction to Magnetochemistry.* Academic Press, London, 1968.

19. König, E., *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds.* Springer-Verlag, Berlin, 1966.
20. van Niekerk, J. N. and Schoening, F. R. L., *Acta Crystallogr. 6,* 227 (1953).
21. de Meester, P., Fletcher, S. R., and Skapski, A. C., *J. Chem. Soc., Dalton Trans. 1973,* 2575.
22. Kato, M., Jonassen, H. B., and Fanning, J. C., *Chem. Rev. 64,* 99 (1964) and citations.
23. Kondo, M. and Kubo, M., *J. Phys. Chem. 62,* 468 (1958).
24. Jensen, K. A. and Nielsen, P. H., *Acta Chem. Scand. 17,* 1875 (1963).
25. Tsuchida, R. and Yamada, S., *Nature* (London) *178,* 1171 (1955).
26. Bleaney, B. and Bowers, K. D., *Proc. Roy. Soc. A214,* 451 (1952).
27. Wasson, R. J., Shyr, C. I., and Trapp, C., *Inorg. Chem. 7,* 469 (1968).
28. Abe, H. and Shimada, J., *J. Phys. Soc. Jap. 12,* 1255 (1957).
29. Felthouse, T. F. and Hendrickson, D. S., *Inorg. Chem. 17,* 2636 (1980).
30. Mroziński, J. and Bukowska-Strzyzewska, M., *J. Mol. Struct. 65,* 277 (1980).
31. Melnik, M., *Coord. Chem. Rev. 42,* 259 (1982).
32. Grasdalen, H. and Svare, I., *Acta Chem. Scand. 25,* 1089 (1971).
33. Gažo, J., *Chem. Zvesti 19,* 826 (1965).