Electron Spin Resonance Study of the Formation of Two Dimeric Species in Bis(1-phenylbutane-1,3-dionato)- and Bis(ethylacetoacetato)-copper(II)

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From the e.s.r. spectra of the title complexes in frozen toluene solutions, it has been found that both form two dimeric species. The spin-exchange interaction energies of the dimers have been determined by measuring the temperature variation of the spectral intensity of the $\Delta M = 2$ transitions over the range 1.6—4.2 K. The dimeric structures have been examined by computer simulation of the dimer e.s.r. spectra and are discussed in relation to two well known types of molecular packing in crystals of planar metal complexes and to the polymorphism displayed by many metal complexes.

A NUMBER of e.s.r. studies on dimer formation in planar copper(II) complexes have been carried out in the last few years.[1-6] In previous papers,[1] we have reported that many β-diketone chelates of Cu^{II} form dimers in toluene, while giving no detailed information on the dimeric structures and exchange coupling. Recently, however, by reinvestigating the same systems in detail, it has been revealed that two dimeric species with different structures coexist in some solutions. This fact is of great interest in connection with the polymorphism displayed by many complexes of β-diketones and their Schiff bases, together with the fact that dimeric structures of some Schiff-base complexes of Cu^{II} are solvent-dependent.[6] In the present paper we report and discuss detailed e.s.r. results for bis(1-phenylbutane-1,3-dionato)copper(II), $[Cu(pbd)_2]$, and bis(ethylacetoacetato)copper(II), $[Cu(eaa)_2]$, in toluene.

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[1] H. Yokoi and T. Isobe, *Bull. Chem. Soc. Japan*, 1971, **44**, 1446; 1973, **46**, 447; H. Yokoi, unpublished work.

[2] J. R. Pilbrow, A. D. Toy, and T. D. Smith, *J. Chem. Soc.* (*A*), 1969, 1029; P. D. W. Boyd, T. D. Smith, J. H. Price, and J. R. Pilbrow, *J. Chem. Phys.*, 1972, **56**, 1253; A. D. Toy, M. D. Hobday, P. D. W. Boyd, and T. D. Smith, *J.C.S. Dalton*, 1973, 1259.

[3] M. Chikira and T. Isobe, *Bull. Chem. Soc. Japan*, 1972, **45**, 3006.

[4] M. Chikira, H. Yokoi, and T. Isobe, *Bull. Chem. Soc. Japan*, 1974, **47**, 2208.

[5] M. Chikira and T. Isobe, *Chem. Letters*, 1974, 865; *Bull. Chem. Soc. Japan*, 1975, **48**, 2052.

[6] H. Yokoi and M. Chikira, *J.C.S. Dalton*, 1975, 2101.

EXPERIMENTAL

Materials.—The complexes used were those which had been prepared and purified previously.[1] Toluene was purified in the usual way.[7]

E.S.R. Measurements.—E.s.r. spectra were recorded over the field range 0—5 000 G * on a Hitachi 771 *X*-band spectrometer at liquid-nitrogen temperature and in the range 4.2—1.57 K. The intra-dimer spin-exchange interaction energy J was evaluated as previously [5,8] from the temperature variation of the spectral intensity for $\Delta M = 2$ transitions using the equation $I = (C/T)[3 + \exp(-J/kT)]^{-1}$, where C is a proportionality constant. Computer simulation was carried out at the Computer Center of Tohoku University on an NEAC 2200 computer using a program based on the point-dipole approximation.[3,5,6]

RESULTS AND DISCUSSION

Dimer E.S.R. Spectra.—The observed e.s.r. spectra of [Cu(pbd)$_2$] and [Cu(eaa)$_2$] in toluene at 77 K are shown as full lines in Figures 1 and 2. From the spectral line shape, it is clear that the half-field spectrum observed for [Cu(pbd)$_2$] in toluene [Figure 2(*a*)] is due to two kinds of $\Delta M = 2$ transitions, *i.e.* two kinds of dimers with different structures are present in solution. On the other hand, the $\Delta M = 1$ spectra [Figure 1(*a*)] clearly show that there are three species, monomers and two kinds of dimers, in solution. In these spectra, signals due to the second dimeric species at both extremities of the spectra were not observed before the spectra were recorded at a high gain. The reason for this is not because the ratio of the spectral intensity of the second to the first dimeric species is lower for $\Delta M = 1$ than for $\Delta M = 2$ transitions, but because the $\Delta M = 1$ spectrum of the second dimeric species covers a wider range than that of the first, and probably because inhomogeneous absorption lines become broader with increasing fine-structure splittings owing to small differences in the structures of the dimers.

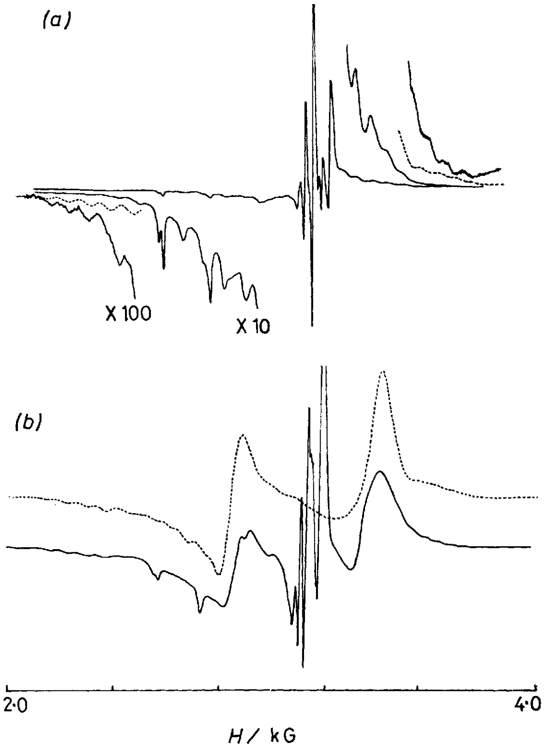

FIGURE 1 *X*-Band e.s.r. spectra of (*a*) [Cu(pbd)$_2$] and (*b*) [Cu(eaa)$_2$] for $\Delta M = 1$ transitions: (——) observed in toluene at 77 K; (– – – –) computer simulated with the parameters listed in the Table

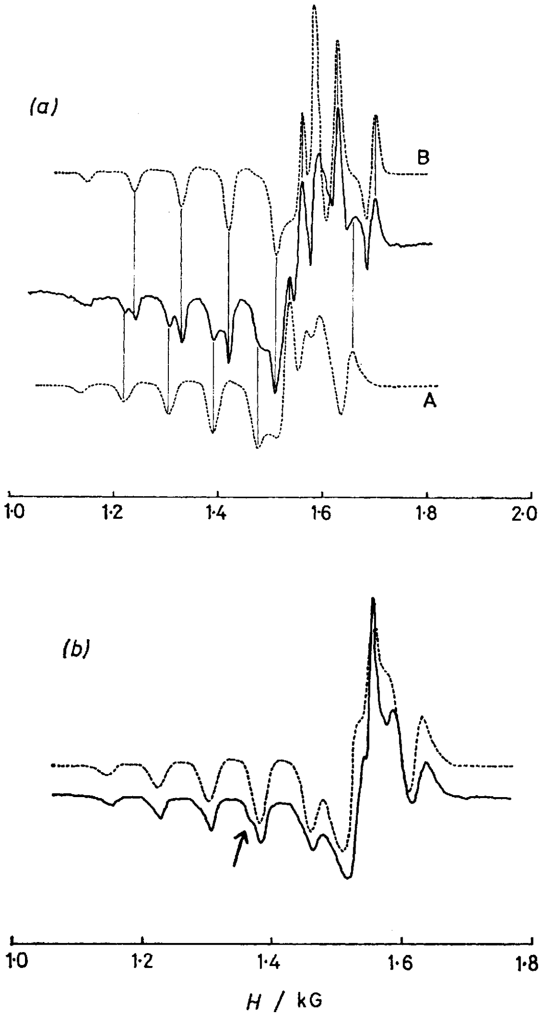

FIGURE 2 *X*-Band e.s.r. spectra of (*a*) [Cu(pbd)$_2$] and (*b*) [Cu(eaa)$_2$] for $\Delta M = 2$ transitions: (——) observed in toluene at 77 K; (– – – –) computer simulated with the parameters listed in the Table. A and B correspond to dimers A and B

The fact that every parallel line in the half-field spectrum of [Cu(eaa)$_2$] in toluene has a shoulder, as shown by an arrow in Figure 2(*b*), similarly indicates that there are two dimeric species in this solution, too. It seems probable that the poor resolution of the hyperfine structure in the $\Delta M = 1$ spectrum is caused by the presence of a low concentration of the second dimeric species. From these spectral shapes, the differences in

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* Throughout this paper: 1 G = 10^{-4} T.

[7] J. A. Riddick and W. B. Bunger, 'Organic Solvents,' Wiley, New York, 1970.

[8] M. Chikira and T. Isobe, *Chem. Phys. Letters*, 1975, **30**, 498.

magnetic parameters between the two dimeric species of $[Cu(eaa)_2]$ are estimated to be small compared with those for $[Cu(pbd)_2]$.

Intra-dimer Spin-exchange Interactions.—Information on the intra-dimer spin-exchange interaction energy J in each dimer is necessary for an evaluation of the dimeric structure by computer simulation.[3,9] The J value was determined as previously,[5,8] measurements being made of the temperature variation of the relative intensities in the $\Delta M = 2$ spectrum. Enlarged absorption lines near 1 400 G at 1.57 and 4.2 K in the half-field spectrum of $[Cu(pbd)_2]$ in toluene are shown in Figure 3. Since the two peaks corresponding to the two dimeric species are well resolved, the temperature variations of their peak heights, H_A and H_B, could be easily measured. On the other hand, there was no temperature dependence of the line shape in the half-field spectrum of $[Cu(eaa)_2]$ in toluene over the range 1.57—4.2 K, indicating that the two dimeric species present in solution have almost the same J values. Accordingly, the temperature variation of the total spectrum height H_C was measured over the same range. Relative changes in H_A, H_B, and H_C in units of their values at 4.2 K are plotted in Figure 4. Full lines shown are the best fits to the experimental plots using the J values listed. These J values indicate that the magnetic interactions are weakly antiferromagnetic as in most salicylaldehyde Schiff-base complexes of Cu^{II} in solution,[5,6,8] suggesting that there is no strong ferromagnetism in these copper pairs. It should be noted that the dimeric species B has the smallest $|J|$ value of all the dimers so far studied. Its J value of -0.3 cm^{-1} corresponds to the Weiss constant of $\theta = -0.53$ K which was determined from the temperature variation of the susceptibility of crystals of bis(pentane-2,4-dionato)copper(II), $[Cu(pd)_2]$;[10] it is noteworthy that this complex shows almost the same dimer spectrum in toluene as the dimeric species B.[1]

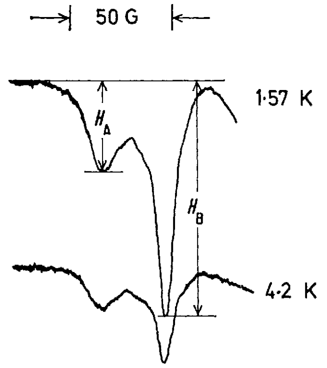

FIGURE 3 Temperature dependence of two peak heights near 1 400 G in the $\Delta M = 2$ spectral region of $[Cu(pbd)_2]$ in toluene

Dimeric Structures.—The $|J|$ value of 0.3 cm^{-1} in the dimeric species B is of the same order of magnitude as the energy of the X-band microwave. In such a case, in order to calculate precisely the resonance magnetic field for $\Delta M = 1$ transitions, the mixing of the singlet and triplet states must be taken into consideration. On the other hand, there is no necessity to take this mixing into account for $\Delta M = 2$ transitions.* In the case of the dimeric species B, then, only the $\Delta M = 2$ spectrum was investigated by the computer-simulation method used previously.[3,5,6] The other dimer spectra were dealt with in the usual way. All the dotted spectra shown in Figures 1 and 2 are the best fits to the observed spectra. We can see from Figure 2(a) that the observed spectrum may be simulated by superimposition of the two dotted spectra. The results are summarized in the Table. Although $[Cu(eaa)_2]$ in toluene originally forms two dimeric species, the differences between the parameters were limited by errors in the simulation procedure (see Table). Here, ξ and r are the angle between the $g_{\parallel}$ axis and the copper–copper axis and the distance between the two copper atoms, respectively, in parallel planar dimers.

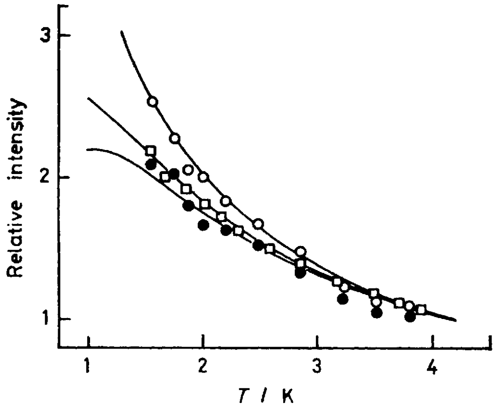

FIGURE 4 Temperature variations of the relative intensities in $\Delta M = 2$ spectra: (●) dimer A ($J = -1.1$ cm^{-1}) and (○) dimer B ($J = -0.3$ cm^{-1}) for $[Cu(pbd)_2]$; (□) dimers ($J = -1.0$ cm^{-1}) for $[Cu(eaa)_2]$

Figure 5 shows two well known types of molecular packing found in many crystals of planar metal com-

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* The spin Hamiltonian for the present dimers can be expressed as in (1) where H_{dd} represents the spin–dipole interaction

$$\mathscr{H} = \beta(\boldsymbol{S}_1 + \boldsymbol{S}_2)\boldsymbol{g}\boldsymbol{H} - J\boldsymbol{S}_1\boldsymbol{S}_2 + (1/2)(\boldsymbol{S}_1 + \boldsymbol{S}_2)\boldsymbol{A}(\boldsymbol{I}_1 + \boldsymbol{I}_2) + (1/2)(\boldsymbol{S}_1 - \boldsymbol{S}_2)\boldsymbol{A}(\boldsymbol{I}_1 - \boldsymbol{I}_2) + H_{dd} \quad (1)$$

operator and the other terms and symbols have their usual meanings. We made perturbation calculations to second order for the last three terms in equation (1). When the singlet and triplet spin functions are written as $\psi^1(0)$ and $\psi^3(-1, 0, 1)$ respectively (M_S values in parentheses), the mixing of these states occurs through non-zero matrix elements of the fourth term between $\psi^1(0)$ and $\psi^3(\pm1)$, where only the A_x and A_y components are operative. The $|A_x|$ and $|A_y|$ values for copper(II) complexes are normally much smaller than the minimum energy difference ($ca.$ 0.15 cm^{-1}) between $\psi^1(0)$ and $\psi^3(-1)$ near fields for $\Delta M = 2$ transitions, so that the mixing of $\psi^1(0)$ and $\psi^3(\pm1)$ is negligibly small. This indicates that $\Delta M = 2$ spectra can be simulated by our method without any changes. On the other hand, for $\Delta M = 1$ transitions there is no reason to neglect mixing effects of the singlet and triplet states, because the mixing of $\psi^1(0)$ and $\psi^3(0)$ occurs through a non-zero matrix element of the A_z component and the energy difference between $\psi^1(0)$ and $\psi^3(-1)$ is remarkably small.

[9] T. D. Smith and J. R. Pilbrow, *Co-ordination Chem. Rev.*, 1974, **13**, 174 and refs. therein.

[10] J. J. Fritz and R. C. Taylor, *J. Amer. Chem. Soc.*, 1958, **80**, 4484.

plexes. In type (I), the carbon atoms of the =CH– groups of neighbouring molecules are situated at the apical positions. Many crystalline β-diketone chelate complexes of Cu^{II}, such as $[Cu(pd)_2]$,[11] $[Cu(pbd)_2]$,[12] and $[Cu(eaa)_2]$,[13] belong to this type. The *X*-ray data of these three complexes lead to values of $r = ca.$ 4.5 Å and $\xi = ca.$ 47° On the other hand, type (II) exhibits a dimeric structure in which the bonding between neighbouring molecules occurs through the oxygen atoms at the apical positions. *NN'*-Ethylenebis(salicylideneiminato)copper(II),[14] bis(*N*-methyl-salicylideneiminato)copper(II) in γ crystalline form,[15] and bis(quinolin-8-olato)copper(II) [16] belong to type (II).

TABLE

Magnetic and structural parameters for the dimeric and monomeric species of $[Cu(pbd)_2]$ and $[Cu(eaa)_2]$ in toluene

Complex	Species	$g_{\parallel}$	$g_{\perp}$	$10^3\lvert A_{\parallel}\rvert$	$10^3\lvert A_{\perp}\rvert$	r	ξ
				cm^{-1}		Å	°
$[Cu(pbd)_2]$	Dimer A	2.265	2.050	8.5	1.0	3.75	35
	Dimer B	2.255	2.050	9.5	1.0	4.60	50
	Monomer	2.255	2.050	9.6 *			
$[Cu(eaa)_2]$	Dimers	2.275	2.055	8.3	1.0	3.75	40
	Monomer	2.282	2.06	8.8 *			

* Value of $\lvert A_{M\parallel}/2\rvert$.

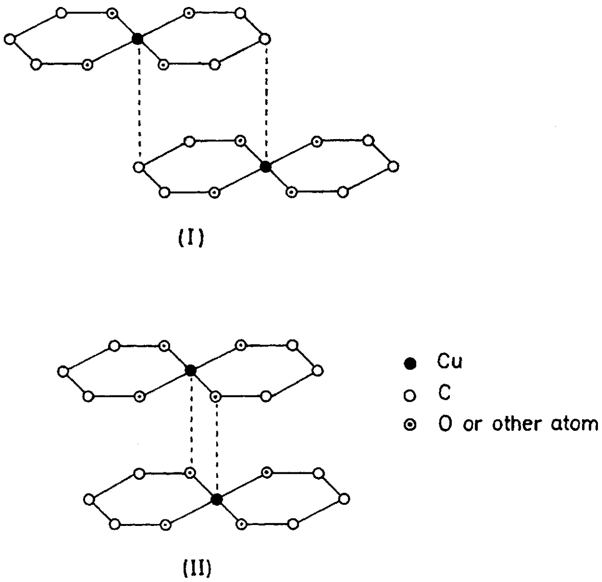

FIGURE 5 Schematically drawn types of dimeric structures

Bis(salicylaldehydato)copper(II), another β-diketone chelate, is of interest because this complex has three crystal modifications, the structures of two of which have been studied by *X*-ray crystallography. One modification obtained on recrystallization from hot ethanol belongs approximately to type (II),[17] although the apical position is occupied not by the oxygen atom but by the delocalized system of the carbonyl group. For this crystal modification, $r = 4.05$ Å and $\xi = 28°$. On the other hand, another modification obtained by crystallization from cold chloroform has the values of $r = 6.4$ Å and $\xi = ca.$ 60°, belonging to type (I).[18]

The dimeric species B corresponds to the cases of crystalline $[Cu(pd)_2]$, $[Cu(pbd)_2]$, and $[Cu(eaa)_2]$ in respect of the values of r and ξ. It follows that species B has a structure of type (I). It has been reported that the $g_{\parallel}$ and $\lvert A_{\parallel}\rvert$ values of planar copper(II) complexes are increased and decreased respectively by strong apical co-ordination.[19,20] Placing of the =CH– group at the apical position is not considered to produce a strong apical ligand-field perturbation. The above conclusion is also supported by the fact that the dimeric species B has the same $g_{\parallel}$ and $\lvert A_{\parallel}\rvert$ values as the monomer (Table). The small $\lvert J\rvert$ value, which is comparable to that of crystalline $[Cu(pd)_2]$, seems to be consistent with the large r value.

On the other hand, the dimeric species A, from the values of r and ξ, seems to be analogous in structure to type (II). The relative orientation of the Cu–Cu and Cu–O axes, however, cannot be deduced by the present simulation method, in which the g and A tensors were assumed to be axial by reference to the e.s.r. results of monomeric $[Cu(pd)_2]$ [21] and $[Cu(pbd)_2]$ [22] in diluted crystals. Therefore, we cannot obtain exact information on the apical co-ordination of the oxygen atoms from data on r and ξ alone. The oxygen atoms, however, are likely to occupy the apical positions in the dimeric species A, because the $g_{\parallel}$ and $\lvert A_{\parallel}\rvert$ values of the dimer are larger and smaller respectively than those of the monomer (Table).

Judging from the values of r and ξ, both dimeric species of $[Cu(eaa)_2]$ in toluene are expected to have structures analogous to type (II). By comparison of the g and A values of the dimers and monomers, however, it

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[11] H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, 1953, **4C**, 43.

[12] P. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, 1966, **5**, 516.

[13] G. A. Barclay and A. Cooper, *J. Chem. Soc.*, 1965, 3746.

[14] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

[15] D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc. (A)*, 1968, 460.

[16] J. A. Bevan, D. P. Graddon, and J. F. McConnell, *Nature*, 1963, **199**, 373.

[17] A. J. McKinnon, T. N. Waters, and D. Hall, *J. Chem. Soc.*, 1964, 3290; D. Hall, A. J. McKinnon, and T. N. Waters, *ibid.*, 1965, 425.

[18] D. E. Sands, 'Introduction to Crystallography,' W. A. Benjamin, New York, 1969, p. 9.

[19] H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Japan*, 1970, **43**, 1078.

[20] J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, 1972, **94**, 4550.

[21] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31.

[22] M. A. Hitchman and R. L. Belford, 'Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Plenum Press, New York, 1969, p. 97.

seems unlikely that the apical co-ordination of oxygen atoms is present in the dimers. At present, it is difficult to say anything about the differences in structure between these two dimeric species, although we can suggest that dimers of both *trans* and *cis* complexes may be formed, but there is no means of verifying this. The *J* values of the dimeric species under discussion and of the dimeric species A are of the same order of magnitude as those in many salicylaldehyde Schiff-base complexes of Cu^{II} in solution, in parallel with the values of *r* and ξ.[5,6,8]

Polymorphism.—Polymorphism is a well known phenomenon displayed by many salicylaldehyde Schiff-base complexes.[23] The polymorphism of bis(salicylaldehydato)copper(II) has been described above. Intuitively, information on dimer formation in solution seems to be useful in considering polymorphism. In a previous study [6] we found that the dimeric structures of many salicylaldehyde Schiff-base complexes of Cu^{II} in solution are affected by small changes in solvent properties. Now, it has been revealed for the first time that two dimeric species can coexist, perhaps at equilibrium,* for some β-diketone chelate complexes in solution. These facts suggest that there are no large differences in stabilization energy between the possible dimeric structures of each complex. The equilibrium between the different dimeric species is considered to depend subtly on the nature of the solvent, temperature, and various other conditions, indicating that dimeric structures are determined by a subtle balance of various kinds of interaction between the monomeric halves of the dimers and between the dimers and solvent. This is reminiscent of the situation encountered in preparing a crystal modification of a complex which displays polymorphism. Dimer formation is regarded as the first step in molecular aggregation which finally leads to the formation of microcrystals. In some cases, the types of dimeric structure formed in solution may be the same as those in crystals, as seen in this study. With respect to polymorphism, it is of great interest that dimer formation takes place in various ways according to the conditions.

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* It has been shown experimentally that there is an equilibrium between the monomer and dimer in dimeric systems (see refs. 1 and 4). A constant e.s.r. intensity ratio between the monomeric and two dimeric species at a given concentration indicates that the two dimeric species are also at equilibrium.

[23] L. M. Shkol'nikova and E. A. Shugan, *Zhur. strukt. Khim.*, 1964, **5**, 590.