

Relation between the Crystal Structures of Some Salts of the Type $Me(OCOCH_3)_2 \cdot nH_2O$ and Their Ability to Form Mixed Crystals or Double Salts ($Me^{2+} = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd$)

CHR. BALAREW AND D. STOILOVA

Chemical Reagents and Preparations Laboratory, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

Received May 26, 1980; in revised form November 19, 1980

An attempt is made to find the relation between the crystal structures of some salts of the type $Me(OCOCH_3)_2 \cdot nH_2O$ ($Me^{2+} = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd$) and their ability to form mixed crystals or double salts by taking into account the difference in the ground-state configurations of the metal (II) ions. Such a treatment is based on the theoretical argument that the formation of isomorphous and isodimorphous mixed crystals occurs when the admixed ion may assume the coordination environment of the substituted ion in the crystal structure of the host salt. Double salts are formed mainly between the acetates of the d^5 , d^{10} and p^6 metal ions, i.e., for ions that allow strong angular deformations of the coordination polyhedra or when at least one of the metal ions meets this condition so that acetate bridge bonding may occur.

Introduction

The processes of cocrystallization in a number of systems of the type $Me(OCOCH_3)_2-Me(OCOCH_3)_2-H_2O$ have been extensively studied (1-8). The present work represents an attempt to find the relation between the crystal structures of the individual salts participating in the systems under consideration and their ability to form mixed crystals or double salts, by taking into account the differences in the ground-state electronic configuration of the metal (II) ions. Such a treatment is based on the theoretical argument that the formation of isomorphous and isodimorphous mixed crystals occurs when the admixed ion may assume the coordination environment of the substituted ion in the crystal structure of the host salt.

Crystal Structures of the Salts of the $Me(OCOCH_3)_2 \cdot nH_2O$ Type

The crystal lattice parameters of the salts of the type $Me(OCOCH_3)_2 \cdot nH_2O$ ($Me^{2+} = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd; n = 4, 2, 1, \text{ or } 0$) are listed in Table I. It is seen from the table that the structures of these salts vary considerably and, in order to explain the differences in these crystal structures, a more detailed treatment is needed. For this purpose, the available data on the Me-O bond lengths and O-Me-O angles in the structures of the salts under consideration are listed in Table II.

According to the acetate bonding type to the metal ions, the crystal hydrates of the metal (II) acetates may be divided into several groups:

—bridge-bonded acetates as those in the

TABLE I
CRYSTAL LATTICE PARAMETERS OF THE SALTS OF THE TYPE $Me(OCOCH_3)_2 \cdot nH_2O$

Parameter	Compound				
	$Mg(OCOCH_3)_2 \cdot 4H_2O$ (Ref. (9))	$Mn(OCOCH_3)_2 \cdot 4H_2O$ (Ref. (10)) (Ref. (11))		$Co(OCOCH_3)_2 \cdot 4H_2O$ (Ref. (12))	$Ni(OCOCH_3)_2 \cdot 4H_2O$ (Ref. (13))
<i>a</i> (Å)	4.75	9.13	11.1	4.77	4.746
<i>b</i> (Å)	11.79	17.62	17.6	11.85	11.711
<i>c</i> (Å)	8.52	19.76		8.42	8.425
β	94°54'	94.5°	118.62°	94°30'	93.6°
<i>Z</i>	2		6	2	2
Space group	$P2_1/c$		$P2_1/c$	$P2_1/c$	$P2_1/c$
	$Zn(OCOCH_3)_2 \cdot 2H_2O$ (Ref. (14))	$Cd(OCOCH_3)_2 \cdot 2H_2O$ (Ref. (15))	$Cu(OCOCH_3)_2 \cdot H_2O$ (Ref. (17))	$Mg(OCOCH_3)_2 \cdot H_2O$ (Ref. (16))	
<i>a</i> (Å)	14.50	8.690	13.168	11.74	
<i>b</i> (Å)	5.32	11.920	8.564	17.54	
<i>c</i> (Å)	11.02	8.100	13.858	6.65	
β	100°		117.02°		
<i>Z</i>	4	4	4		
Space group	$C2/c$	$P2_12_12_1$	$C2/c$		
	$Mg(OCOCH_3)_2$ (Ref. (16))		$Zn(OCOCH_3)_2$ (Ref. (19))		
	α form	β form			
<i>a</i> (Å)	11.27	10.34	10.92		
<i>b</i> (Å)	15.04	12.35			
<i>c</i> (Å)	10.99	7.726			
α		103°27'			
β		14°32'			
γ		81°03'			

dimer of the copper acetate monohydrate and manganese acetate tetrahydrate.

—bidentate-bonded acetates as those in the zinc and cadmium acetate dihydrates.

—unidentate-bonded acetates as those in the magnesium, cobalt, and nickel acetate tetrahydrates.

The oxygen octahedron about Cu^{2+} in the structure of the copper acetate monohydrate dimer is strongly distorted: four oxygen atoms from the bridging acetate ions located at the corners of a square are the closest neighbors of Cu^{2+} . A water molecule and a second copper atom are located

normal to the plane of four oxygen atoms. The longest bond in the octahedra ($Cu-Cu = 2.616 \text{ \AA}$) and the shortest bond ($Cu-O = 1.945 \text{ \AA}$) differ considerably ($\Delta = 0.671 \text{ \AA}$) and this difference is the major factor defining the strong distortion of the octahedron about Cu^{2+} (17).

There are two types of manganese ions, located at sites of different symmetry, in the structure of the manganese acetate tetrahydrate. One type of the manganese ions is surrounded by six oxygen atoms pertaining to six acetate ions bridging the metal ions to the second type of manganese ions.

TABLE II
 $Me-O$ BOND LENGTHS AND $O-Me-O$ ANGLES IN THE STRUCTURES OF SOME ACETATES

$Mg(OCOCH_3)_2 \cdot 4H_2O$		$Co(OCOCH_3)_2 \cdot 4H_2O$		$Ni(OCOCH_3)_2 \cdot 4H_2O$	
$Mg-O_{O_1}$	2.11	$Co-O_{O_1}$	2.12	$Ni-O_{O_1}$	2.068
$Mg-O_{w_1}$	2.08	$Co-O_{w_1}$	2.11	$Ni-O_{w_1}$	2.081
$Mg-O_{w_2}$	2.07	$Co-O_{w_2}$	2.06	$Ni-O_{w_2}$	2.048
$Mg-O_m$	2.09	$Co-O_m$	2.09	$Ni-O_m$	2.065
$O_1-Mg-O_{w_1}$	$90^\circ 48'$	$O_2-Co-O_{w_1}$	$90^\circ 44'$	$O_1-Ni-O_{w_1}$	89.8°
$O_{w_1}-Mg-O_{w_2}$	$88^\circ 48'$	$O_1-Co-O_{w_2}$	$90^\circ 33'$	$O_1-Ni-O_{w_2}$	90.8°
				$O_{w_1}-Ni-O_{w_2}$	91.6°
$Zn(OCOCH_3)_2 \cdot 2H_2O$		$Cd(OCOCH_3)_2 \cdot 2H_2O$		$Cu(OCOCH_3)_2 \cdot H_2O$	
$Zn-O_{O_1}$	2.18	$Cd-O_1$	2.597	$Cu_1-O'_1$	1.986
$Zn-O_{O_2}$	2.17	$Cd-O_2$	2.294	Cu_1-O_2	1.994
$Zn-O_{w_1}$	2.14	$Cd-O_3$	2.304	$Cu_1-O'_3$	1.945
$Zn-O_m$	2.16	$Cd-O_4$	2.546	Cu_1-O_4	1.950
		$Cd-O_{w_1}$	2.325	Cu_1-O_5	2.156
O_1-Zn-O_2	61°	$Cd-O_{w_2}$	2.299	$Cu_1-Cu'_1$	2.616
O_1-Zn-H_2O	103°	$Cd-O'_1$	2.297	$Cu-O_m(ac)$	1.969
$O_1-Zn-O'_1$	158°	$Cd-O_m$	2.379		
$O_1-Zn-O'_2$	104°			$O_5-Cu_1-O'_1$	98.4°
O_2-Zn-H_2O	96°	$O_1-Cd-O'_1$	133.8°	$O_5-Cu_1-O_2$	93.0°
$H_2O-Zn-H_2O$	94°	O_1-Cd-O_2	52.7°	$O_5-Cu_1-O'_3$	97.7°
$O_2-Zn-O'_2$	85°	O_1-Cd-O_3	79.3°	$O_5-Cu_1-O_4$	93.3°
$H_2O-Zn-O'_1$	92°	O_1-Cd-O_4	129.6°	$O'_1-Cu_1-O_2$	168.6°
$H_2O-Zn-O'_2$	152°	O_3-Cd-O_4	53.6°	$O'_1-Cu_1-O'_3$	87.5°
		$H_2O-Cd-H_2O$	83.1°	$O'_1-Cu_1-O_4$	91.1°
				$O_2-Cu_1-O'_3$	90.1°
				$O_2-Cu_1-O_4$	89.1°
				$O'_3-Cu_1-O_4$	168.9°

The coordination polyhedron about the second type of manganese ions is built up of two oxygen atoms from two water molecules and four oxygen atoms from four acetate ions in a bridging position (10, 11). There are, however, no literature data on the Mn-O bond lengths and O-Mn-O bond angles in the structure of $Mn(OCOCH_3)_2 \cdot 4H_2O$.

The oxygen octahedron in the zinc acetate dihydrate is built up of two oxygen atoms pertaining to two water molecules and four oxygen atoms from two bidentate acetate ions. The Zn-O bond lengths in the structure of zinc acetate dihydrate are equal; the O-Zn-O bond angles, however,

deviate strongly from 90° , which brings about a considerable distortion of the oxygen octahedron (14).

The Cd^{2+} in the structure of cadmium acetate dihydrate is surrounded by seven oxygen atoms: two oxygen atoms from two water molecules, four oxygen atoms from two bidentate acetate ions, and the oxygen atom from an acetate ion bridging the neighboring cadmium acetate molecule. The distortion of the oxygen polyhedron is due to the O-Cd-O angles values, which are far from 90° , and to the Cd-O bond length differences for the bidentate ions ($\Delta = 0.30 \text{ \AA}$) (15).

The unidentate-bonded acetates (Mg,

Co, and Ni acetate tetrahydrates) have an oxygen octahedron built up of four oxygen atoms from four water molecules and two oxygen atoms from two acetate ions. The approximately equal $Me-O$ bond lengths as well as the $O-Me-O$ bond angles (close to 90°) locate the ligand atoms in a comparatively regular octahedral arrangement about the metal ions (9, 12, 13).

The following conclusions may be drawn on the basis of the above considerations, supported also by the experimental data on the formation of mixed crystals and double salts in acetate systems (*vide infra*):

Bidentate acetate ligands are observed when the metal-ion polyhedron may be subjected to a strong angular deformation ($O-Me-O$ valent angle deformation). This occurs in the presence of d^{10} ions (Zn^{2+} and Cd^{2+}) and it is also possible in the high-spin d^5 configuration (Mn^{2+}). In these cases, the $O-Me-O$ angles of the bidentate acetate ion deviate strongly from 90° . Moreover, the larger the ionic radius of Me^{2+} , the smaller this angle (52.7° for Cd^{2+} and 61° for Zn^{2+}). The bidentate bond formation is favored additionally by the higher extent of covalency of the metal-ligand bond. As is known, the d^{10} ions are the strongest complex-forming reagents with respect to oxygen-containing ligands, and for their acetates bidentate bonding is observed. The p^6 ions (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}), despite their ability to endure strong angular deformation without loss of energy, due to the higher extent of ionicity of the $Me-O$ bonds, do not form bidentate bonds with the acetate ions (Table III).

The d^{6-8} ions (Fe^{2+} , Co^{2+} , Ni^{2+}), due to loss of crystal field stabilization energy (the $O-Me-O$ angles are close to 90° , when the overlap between ligand orbitals and metal d orbitals is most favorable), give only unidentate bonds with the acetate ions.

The d^4 and d^9 ions (Cu^{2+} , Cr^{2+} , Mo^{2+} , and W^{2+}), displaying strong radial deformations

TABLE III
DEGREE OF IONICITY FOR THE
BONDING $Me-O$ FOR SOME
METAL(II) IONS (29)

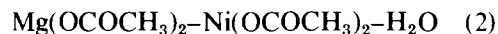
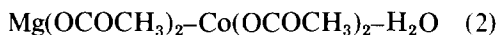
$Me-O$	Degree of ionicity (%)
Mg-O	73.4
Ca-O	79.0
Sr-O	79.0
Ba-O	81.5
Mn-O	66.8
Cr-O	66.8
Fe-O	55.5
Co-O	55.5
Ni-O	51.4
Zn-O	63.2
Cd-O	63.2
Pb-O	59.4
Cu-O	43.0

(large differences between the separate $Me-O$ bond lengths as a consequence of the Jahn-Teller effect), form dimeric molecules with $Me-Me$ bonds; the two metal ions in the dimeric molecule are bridged by acetate ions (17, 18, 20-22).

Formation of Mixed Crystals between the Metal Acetates

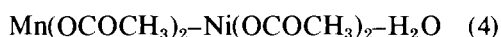
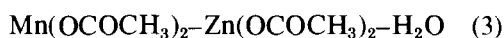
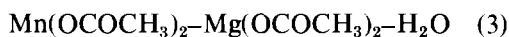
The results obtained from cocrystallization studies on acetate systems may be used to divide these systems into two major groups:

1. Systems in which a continuous series of mixed crystals (isomorphous substitution) is formed

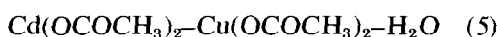
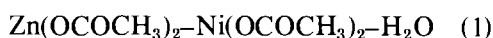
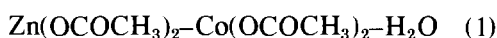


2. Systems in which a discontinuous series of mixed crystals (isodimorphous substitution) is formed. This group is subdivided further.

2.1. Two series of mixed crystals are formed:



2.2 A simple salt and mixed crystals are formed:



As mentioned in the Introduction the formation of mixed crystals is related to the possibility of the admixed ion to assume the coordination environment that is typical for the metal ion of the host crystal. Obviously, this possibility is defined by the ground-state electronic configuration of the metal ion, which on its turn defines the possibility of angular and/or radial deformation of the oxygen polyhedron about the metal ion.

The formation of a continuous series of mixed crystals is typical for the isostructural nickel, cobalt, and magnesium acetate tetrahydrates.

The Co^{2+} and Ni^{2+} ions in an octahedral ligand field have ground-state configurations $t_{2g}^5e_g^2$ and $t_{2g}^6e_g^2$, respectively; deformation of the oxygen polyhedron cannot occur without loss of crystal field stabilization energy (the bond lengths $Me-O$ are equal and the valent angles $O-Me-O$ are approximately equal to 90° , and for this reason these ions cannot be incorporated into the distorted site of Zn^{2+} . The incorporation of Co^{2+} and Ni^{2+} ions is observed only in the crystals of $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$. Unfortunately there are no literature data on the $Mn-O$ bond lengths and $O-Me-O$ angles. It may be thus assumed that at least one of the oxygen octahedral sites of Mn^{2+} is regular both with respect to the $Mn-O$ bond lengths and with respect to the $O-Mn-O$

angles and may accept Co^{2+} and Ni^{2+} in the $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals.

The Zn^{2+} ions may be incorporated isodimorphously in the $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals by assuming the coordination environment of Co^{2+} and Ni^{2+} (unidentate acetates). Isodimorphous incorporation of Zn^{2+} is also observed in the crystals of $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, in whose structure the acetate ions are bridging. Zn^{2+} ($t_{2g}^6e_g^4$) allows a strong angular distortion of its octahedral site and for this reason it may adopt unidentate bonding coordination (the angles $O-Me-O$ are equal to 90°). Zn^{2+} may replace both Mn_1^{2+} and Mn_2^{2+} irrespective of the extent of regularity of the oxygen octahedron.

The Mn^{2+} ions ($t_{2g}^5e_g^2$), similar to Zn^{2+} , ions allow an angular deformation of their octahedral site and for this reason may be incorporated isodimorphously in the $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals (regular octahedra) and in the $\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ crystals (anregular octahedron).

The Cd^{2+} ions ($t_{2g}^6e_g^4$), similar to Zn^{2+} and Mn^{2+} ions, allow an angular deformation but there are also radial deformations in the Cd^{2+} oxygen polyhedron ($\Delta = 0.30 \text{ \AA}$) due to the higher coordination number of Cd^{2+} (seven) and the bridging position of one of the bidentate acetate group. The presence of radial deformation probably defines, in this case, the incorporation of Cd^{2+} in the $2\text{Cu}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ crystals.

The ground-state electronic configuration of Cu^{2+} ions ($t_{2g}^6e_g^3$) requires a radial deformation of the Cu^{2+} oxygen polyhedron, which on its turn leads to the formation of a Cu-Cu bond. For this reason the Cu^{2+} ions in copper acetate monohydrate cannot be substituted by Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , or Zn^{2+} ions since these ions, due to their smaller ionic radius, as compared with that of Cd^{2+} ions, cannot endure such a strong

radial deformation of the oxygen polyhedron in such wide limits. Cu^{2+} ions cannot replace any of the ions listed above since these ions have almost equal $Me-O$ bond lengths in their structures, and Cu^{2+} ions are strongly subjected to the Jahn-Teller effect. Thus the incorporation of Cu^{2+} ions would result in a considerable strain in the crystal lattices of these salts and loss of crystal field stabilization energy.

The results of studies on the cocrystallization of the systems $\text{Mg}(\text{OCOCH}_3)_2 \cdot \text{Zn}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ (6) and $\text{Mg}(\text{OCOCH}_3)_2 \cdot \text{Cd}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ (3) have shown that Mg^{2+} ions cannot replace isodimorphously Zn^{2+} and Cd^{2+} ions in their acetate dihydrates or, alternatively, they cannot assume the coordination of a metal ion with bidentate ligands. If the lack of bidentate bonds with Mg^{2+} is attributed to the smaller ionic radius of Mg^{2+} this would define a larger O-Mg-O bite angle. To calculate this angle, we assume that the O-O distance in the COO group is 2.20 Å (such is the O-O bond length in Zn and Cd acetate dihydrates) and that the Mg-O bond length is 2.11 Å (this corresponds to the Mg-O distance in $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$). The bite angle calculated under these assumptions is 62.8°; i.e., it is close to O-Zn-O (61°). Consequently, the smaller ionic radius of Mg^{2+} cannot increase considerably the bite angle, and therefore it cannot be the reason for the lack of bidentate bonds in this case.

On the other hand, when studying the systems $\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ (8), $\text{Cd}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ (3), $\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Ba}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ (27), it is found that Ca^{2+} and Ba^{2+} ions cannot isodimorphously replace the Zn^{2+} and Cd^{2+} ions, respectively, in their acetates dihydrates. Studies on the systems $\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Pb}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Cd}(\text{OCOCH}_3)_2 \cdot \text{Pb}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ have shown that Pb^{2+} ions, despite their large ionic radius can substitute isodimorphously

Zn^{2+} and Cd^{2+} ions (28). Hence the reason for the lack of bidentate bonds in the Mg, Ca, and Ba acetates is probably the higher extent of ionicity of the $Me-O$ bonds, whereas for Pb^{2+} ions the ionicity of the Pb-O bond is close to that of Zn^{2+} and Cd^{2+} ions (Table III).

Formation of Double Salts by Metal Acetates

The available data on double salts of metal (II) acetates are collected in Table IV. The double salts $\text{Cd}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot 6\text{H}_2\text{O}$ have bidentate and bridging acetate ions (24, 25).

It is seen from the table that double salts are formed mainly between the acetates of the d^5 , d^{10} , and p^6 metal ions, i.e., for ions that allow strong angular deformation of the coordination polyhedra or when at least one of the metal ions meets this condition so that acetate bridge bonding may occur. Consequently, to form double salts, the two metal ions, or at least one of them, should be a d^5 , d^{10} , or p^6 ion, allowing angular deformations. The differences in the ionic radii favor additionally the formation of double salts, since in such cases the formation of mixed crystals is energetically unprofitable. A similar relationship has been found also for the formation of double salts in chloride systems with the participation of the same metal ions (26).

TABLE IV
COMPOSITION OF THE DOUBLE SALTS

Temperature (°C)	Composition	Reference
25	$\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$	(6)
25	$\text{Cd}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot 6\text{H}_2\text{O}$	(3)
25	$\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{Ca}(\text{OCOCH}_3)_2 \cdot 6\text{H}_2\text{O}$	(5)
25	$\text{Cd}(\text{OCOCH}_3)_2 \cdot \text{Mg}(\text{OCOCH}_3)_2 \cdot 6\text{H}_2\text{O}$	(3)
20	$\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Ba}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$	(27)
60	$\text{Zn}(\text{OCOCH}_3)_2 \cdot \text{Mn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$	(23)

References

1. CHR. BALAREW AND D. STOILOVA, *Comm. Dept. Chem. Bulg. Acad. Sci.* **7**, 355 (1974).
2. CHR. BALAREW AND D. STOILOVA, *C.R. Acad. Bulg. Sci.* **27**, 803 (1974).
3. CHR. BALAREW AND D. STOILOVA, *Zh. Neorg. Khim.* **21**, 555 (1976).
4. D. STOILOVA, CHR. BALAREW, AND L. DEMIREV, *Comm. Dept. Chem. Bulg. Acad. Sci.* **9**, 604 (1976).
5. D. STOILOVA AND V. VASSILEVA, *Comm. Dept. Chem. Bulg. Acad. Sci.* **12**, 562 (1979).
6. CHR. BALAREW AND D. STOILOVA, *C.R. Acad. Bulg. Sci.* **27**, 651 (1974).
7. CHR. BALAREW, D. STOILOVA, AND D. GRIGOROVA, *Jahrb. Hochschule Chem. Tech. Burgas* **9**, 255 (1972).
8. CHR. BALAREW AND D. STOILOVA, *Jahrb. Hochschule Chem. Tech. Burgas* **10**, 503 (1973).
9. J. SHANKAR, P. G. KHUBCHANDANI, AND V. M. PADMANBHAN, *Proc. Indian Acad. Sci. A* **45**, 117 (1957).
10. I. TSUJIKAWA, *J. Phys. Soc. Japan* **18**, 1407 (1963).
11. P. BURLET, P. BURLET, AND E. F. BERTANT, *Solid State Commun.* **14**, 665 (1974).
12. J. N. VAN NIEKERK AND F. R. L. SCHOENING, *Acta Crystallogr.* **6**, 609 (1953).
13. T. C. DOWNIE, W. HARRISON, E. S. RAPER, AND M. A. HEPWORTH, *Acta Crystallogr. Sect. B* **27**, 706 (1971).
14. J. N. VAN NIEKERK, F. R. L. SCHOENING, AND J. M. TALBOT, *Acta Crystallogr.* **6**, 720 (1953).
15. W. HARRISON AND J. TROTTER, *J. Chem. Soc. Dalton*, 956 (1972).
16. WALTER-LEVY, *Compt. Rend.* **249**, 1234 (1959).
17. P. MEESTER, ST. R. FLETCHER, AND A. C. SKAPSKI, *J. Chem. Soc. Dalton*, 2575 (1973).
18. R. CHIDAMBARAM AND G. M. BROWN, *Cryst. Struct. Commun.* **1**, 269 (1973).
19. K. N. SEMENENKO, *Zh. Neorg. Khim.* **3**, 1467 (1958).
20. J. N. VAN NIEKERK AND F. R. L. SCHOENING, *Acta Crystallogr.* **6**, 501 (1953).
21. G. HOLSTE, *Z. Anorg. Allg. Chem.* **398**, 249 (1973).
22. D. LAWTON AND R. MASON, *J. Amer. Chem. Soc.* **87**, 921 (1965).
23. D. STOILOVA, *Z. Anorg. Allg. Chem.* **463**, 227 (1980).
24. D. A. LANGS AND C. R. HARE, *Chem. Commun.* 890 (1970).
25. G. GLIEMANN AND P. MORYS, *Z. Phys. Chem.* **243**, 281 (1970).
26. CHR. BALAREW AND D. SPASSOV, *Zh. Neorg. Khim.* **25**, 2814 (1980).
27. D. STOILOVA, to be published.
28. D. STOILOVA AND CHR. BALAREW, to be published.
29. L. PAULING, "The Nature of the Chemical Bond," 3d ed., Ithaca, N.Y., Cornell University Press, 1960, p. 98.