

Magnetochemical behaviour of polymeric chloroalkoxotitanium(III) compounds

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Dedicated to Academician V. Kellö on his 60th birthday

The magnetic properties of chloroalkoxotitanium(III) compounds formed in the course of thermal decomposition of chloro(aliphatic alcohol)titanium(III) complexes ($C_nH_{2n+1}OH$; $n = 1-4$) were studied. These products were of nonstoichiometric composition and showed anomalously lowered values of effective magnetic moments even at room temperature. The experimentally obtained values of μ_{eff} in the temperature range 77—300 K were interpreted using the Ising model of linear antiferromagnetism and on the basis of this the polymeric structure with antiferromagnetic intramolecular exchange between neighbouring Ti(III) atoms was proposed.

Были изучены магнитные свойства хлоралкоксосоединений титана(III), которые образуются при термическом разложении хлорокомплексов титана(III) с алифатическими алкоголями $C_nH_{2n+1}OH$ ($n = 1-4$) в качестве лигандов. Образовались продукты переменного состава, у которых значения эффективных магнитных моментов были anomalously понижены уже при комнатной температуре. Значения эффективных магнитных моментов, найденных экспериментально в области температур 77—300 К, интерпретировались при помощи модели линейного антиферромагнетизма Исинга, на основании чего можно для них предполагать полимерную структуру с антиферромагнитным внутримолекулярным обменом между отдельными атомами титана(III).

Two groups of Ti(III) compounds, classified on the basis of their magnetic properties are supposed to exist. The one group consists of Ti(III) compounds exhibiting the values of effective magnetic moments in the range 1.73—1.86 B.M., the other one comprises Ti(III) compounds with μ_{eff} anomalously lowered. As it is known to this mentioned second group belong also several chloroalkoxotitanium(III) compounds prepared either directly [1—3] or by thermal decomposition of chloro(aliphatic alcohol)titanium(III) complexes [4—7].

The methoxide compound $\text{Ti}(\text{OCH}_3)_3$ [1] prepared directly was diamagnetic and according to the authors this is the consequence of a very strong interaction between the metal atoms. On the basis of cryomagnetic data the trimeric structure with bridging methoxide groups was proposed for the methoxide $\text{TiCl}_2(\text{OCH}_3) \cdot 2\text{CH}_3\text{OH}$ [2]. The diamagnetic methoxide and ethoxide $\text{Ti}(\text{III})$ compounds of octahedral arrangement and polymeric structure with bridging alkoxide groups are described in [3]. *Giggenbach et al.* [4] studied the $\text{Ti}(\text{III})$ methoxide compounds of intermediate composition formed by thermal decomposition of chlorotitanium(III) complexes with methyl alcohol. The experimental data indicate the formation of the diamagnetic six coordinate polymeric species and a simultaneous release of HCl and the formation of CH_3O^- ions.

As we reported in our previous papers [6, 7], in the course of the thermal decomposition of chloro(aliphatic alcohol)titanium(III) complexes the partial alcoholysis and formation of solid products of nonstoichiometric composition were assumed to take place. Presumably in the course of the above reaction the monomeric units of parent complexes are joining and the new polymeric structural arrangement containing alkoxo groups is formed. The formation of such polymeric species should cause an evident change in magnetic properties and so it seems to be possible to use them to confirm the proposed scheme of thermal decomposition.

Experimental

The parent complexes were prepared in the direct way by the reaction of $\alpha\text{-TiCl}_3$ with corresponding alcohol (methyl alcohol, ethyl alcohol, n- and isopropyl alcohol, n- and isobutyl alcohol) in medium of noncoordinating solvent under dry nitrogen atmosphere [5, 7]. The course of their thermal decomposition in the temperature range 40—400°C was studied [5, 7] and on the basis of the obtained results the products of thermal decomposition were prepared by the procedure described in [8]. The composition of these products of thermal decomposition is variable in a small extent in dependence on experimental conditions.

$\text{Ti}(\text{III})$ was determined cerimetrically using ferroin as an indicator, $\text{Ti}(\text{IV})$ gravimetrically as TiO_2 , Cl^- by the Volhard method, C, H by elemental analysis.

Magnetic measurements were carried out in the temperature range 77—300 K by the Gouy method as it is described in [9].

E.s.r. spectra were recorded at room temperature as well as at 103 K on Varian E-4 in X band.

In the temperature range 77—300 K the magnetic properties of alkoxo compounds prepared as described above were studied:

Parent complexes: $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$, $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$, $\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$, $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$, $\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$, $\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$.

Products of thermal decomposition:

$\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$

Table 1

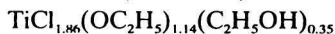
Magnetic susceptibilities and effective magnetic moments of studied chloroalkoxotitanium(III) compounds

$\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$											
T/K	81	92	112	135	154	177	207	233	254	273	295
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	3947	3524	2956	2520	2242	2011	1748	1585	1474	1387	1304
$\mu_{\text{eff}}/\text{B.M.}$	1.43	1.44	1.45	1.47	1.49	1.51	1.52	1.54	1.55	1.55	1.57
$\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$											
T/K	138	201	230	244	256	267	291				
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	177	137	164	164	162	150	137				
$\mu_{\text{eff}}/\text{B.M.}$	0.39	0.42	0.49	0.50	0.51	0.51	0.51				
$\text{TiCl}_{1.86}(\text{OC}_2\text{H}_5)_{1.14}(\text{C}_2\text{H}_5\text{OH})_{0.35}$											
T/K	77	61	180	205	224	237	250	262	272	287	293
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	150	170	166	142	138	142	131	136	136	131	131
$\mu_{\text{eff}}/\text{B.M.}$	0.27	0.42	0.43	0.43	0.44	0.46	0.46	0.48	0.49	0.49	0.50
$\text{TiCl}_{1.60}(\text{OC}_3\text{H}_7)_{1.40}$											
T/K	82	102	121	147	171	193	217	247	273	295	
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	231	227	224	222	219	219	219	217	219	217	
$\mu_{\text{eff}}/\text{B.M.}$	0.34	0.38	0.42	0.46	0.50	0.52	0.55	0.58	0.62	0.64	
$\text{TiCl}_{1.40}(\text{i-OC}_3\text{H}_7)_{1.60}$											
T/K	201	207	230	247	273	282	290				
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	177	170	191	213	213	213	213				
$\mu_{\text{eff}}/\text{B.M.}$	0.48	0.47	0.53	0.58	0.61	0.62	0.63				
$\text{TiCl}_{1.55}(\text{OC}_4\text{H}_9)_{1.45}$											
T/K	175	194	220	247	274	293					
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	230	193	196	188	167	184					
$\mu_{\text{eff}}/\text{B.M.}$	0.51	0.49	0.53	0.54	0.54	0.59					
$\text{TiCl}_{1.70}(\text{i-OC}_4\text{H}_9)_{1.30}$											
T/K	77	112	145	201	213	231	244	258	273	281	293
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	208	192	221	192	187	195	181	181	181	179	187
$\mu_{\text{eff}}/\text{B.M.}$	0.32	0.37	0.45	0.50	0.50	0.53	0.53	0.55	0.56	0.57	0.59

(prepared at 100°C in nitrogen atmosphere, analysis: 19.44% Ti(III), 19.57% Ti (gravim.), 38.73% Cl, 15.82% C, 5.11% H).

$\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$

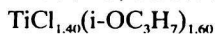
(prepared at 170°C in nitrogen atmosphere, analysis: 28.70% Ti(III), 28.60% Ti (gravim.), 37.09% Cl, 9.84% C, 2.41% H).



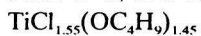
(prepared at 125°C in vacuum, analysis: 26.33% Ti(III), 26.60% Ti (gravim.), 36.28% Cl, 22.40% C, 4.82% H).



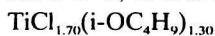
(prepared at 120°C in vacuum, analysis: 24.39% Ti(III), 24.52% Ti (gravim.), 29.22% Cl, 21.70% C, 7.08% H).



(prepared at 120°C in vacuum, analysis: 25.07% Ti(III), 24.59% Ti (gravim.), 26.61% Cl, 30.69% C, 6.43% H).



(prepared at 120°C in vacuum, analysis: 22.32% Ti(III), 23.11% Ti (gravim.), 26.80% Cl, 35.49% C, 7.43% H).



(prepared at 120°C in vacuum, analysis: 22.45% Ti(III), 22.43% Ti (gravim.), 28.71% Cl, 38.29% C, 7.40% H).

The obtained magnetochemical data are presented in Table 1.

Discussion

In comparison with the group of parent alcoholic complexes [9] the products of their thermal decomposition show markedly lowered values of effective magnetic moments. Since no oxidation of Ti(III) to Ti(IV) took place (the determined amounts of Ti(III) within experimental errors agreed with the theoretically predicted values), the anomalously lowered values of μ_{eff} could indicate magnetic interaction between paramagnetic centres as a consequence of polymeric structure formation.

There is a close analogy between this anomalous magnetic behaviour of Ti(III) compounds and that of much better understood polynuclear Cu(II) compounds. Here, too, isolated pairs of metal atom interact to form a lower singlet state ($S = 0$, diamagnetic) and a slightly higher triplet state ($S = 1$, paramagnetic) at the distance J (cm^{-1}). In contrast to copper(II) compounds the magnetochemistry of Ti(III) compounds is not so well developed, which among others may be caused by the fact that nearly all Ti(III) compounds are very sensitive towards oxygen and moisture and thus a slight deficiency in attention may cause certain mistakes in theoretical interpretation. In some cases of Ti(III) compounds it is also possible to explain the interaction using the known equation for singlet—triplet separation for central ions containing one unpaired electron [10—12]. This interpretation could not be applied for the group of compounds discussed in the present paper. The Ising model which describes interactions between an infinite linear chain of paramagnetic atoms is one type of lattice exchange interaction that can be applied to some transition metal complexes [13]. This model has been successfully applied to

oxovanadium(IV) acetate [14], to copper(II) chloride and methoxide [15] as well as to ferromagnetic and antiferromagnetic interactions in polynuclear copper(II) complexes [16]. If $S = 1/2$ for each member of the chain, the Ising model yields expressions for the magnetic susceptibilities parallel (χ_{\parallel}) and perpendicular (χ_{\perp}) to the magnetic field direction

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT} e^{J/kT} \quad (1)$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J} [\tan hK + K \sec h^2 K] \quad (2)$$

where $K = \frac{J}{kT}$.

The average susceptibility ($\chi'_M = \frac{1}{3} \chi'_{\parallel} + \frac{2}{3} \chi'_{\perp}$) is given by the equation

$$\chi'_M = \frac{Ng^2\beta^2}{12kT} \cdot \frac{e^{4K} + (2 + K^{-1}) e^{2K} - K^{-1} e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} \quad (3)$$

The experimentally obtained magnetochemical data for the group of investigated chloroalkoxotitanium(III) compounds can be compared with the theoretical curves computed on the basis of the equation

$$\mu_{\text{eff}} = \frac{g}{2} \left[\frac{e^{4K} + (2 + K^{-1}) e^{2K} - K^{-1} e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} \right]^{1/2} \quad (4)$$

Plots of μ_{eff} vs. temperature are shown in Figs. 1—7, the obtained results are listed in Table 2. The values of J are presented in both systems of units as to be better compared with the previous results. Theoretical curves were computed on Siemens 4004/150 H, the g values were verified by means of e.s.r. spectra.

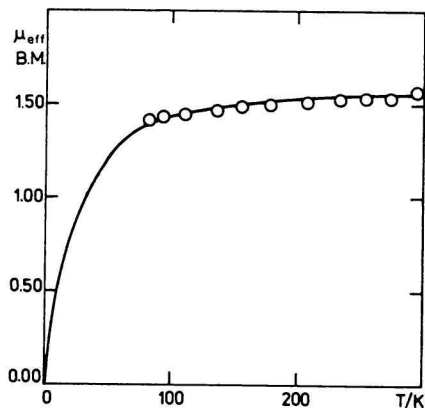


Fig. 1. Dependence of μ_{eff} on T for $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$.
 ○ ○ Experimental points;
 — theoretical curve
 ($g = 1.89, J = -25 \text{ cm}^{-1}$).

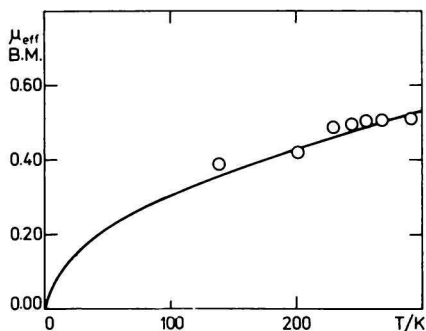


Fig. 2. μ_{eff} vs. T for $\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$.

○ ○ Experimental points;
 — theoretical curve
 ($g = 1.93, J = -700 \text{ cm}^{-1}$).

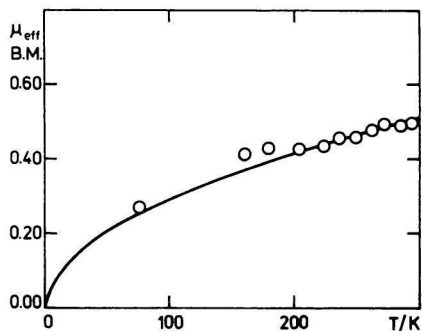


Fig. 3. Dependence of μ_{eff} on T for $\text{TiCl}_{1.86}(\text{OC}_2\text{H}_5)_{1.14}(\text{C}_2\text{H}_5\text{OH})_{0.35}$.

○ ○ Experimental points;
 — theoretical curve
 ($g = 1.94, J = -750 \text{ cm}^{-1}$).

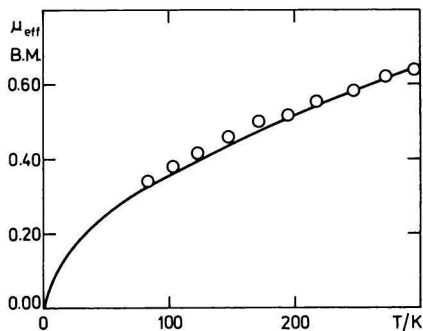


Fig. 4. μ_{eff} vs. T for $\text{TiCl}_{1.60}(\text{OC}_3\text{H}_7)_{1.40}$.

○ ○ Experimental points;
 — theoretical curve
 ($g = 1.92, J = -490 \text{ cm}^{-1}$).

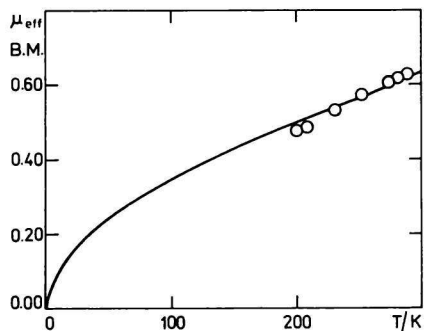


Fig. 5. μ_{eff} vs. T for $\text{TiCl}_{1.40}(\text{i-OC}_3\text{H}_7)_{1.60}$.

○ ○ Experimental points;
 — theoretical curve
 ($g = 1.92, J = -520 \text{ cm}^{-1}$).

One of possible applications of the Ising model [17] is shown in eqn (1) rewritten as

$$\log \left(\frac{4k}{N\beta^2} \chi'_M T \right) = 2 \log g + \frac{J}{kT} \quad (5)$$

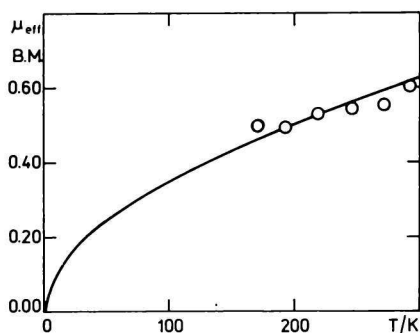


Fig. 6. μ_{eff} vs. T for $\text{TiCl}_{1.55}(\text{OC}_4\text{H}_9)_{1.45}$.

○ ○ Experimental points;

— theoretical curve

($g = 1.95, J = -580 \text{ cm}^{-1}$).

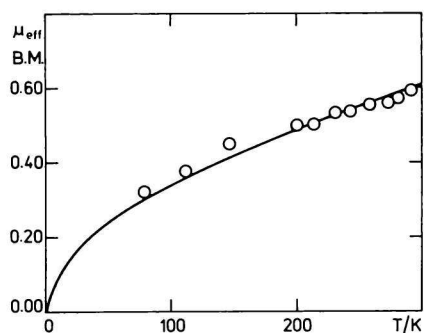


Fig. 7. μ_{eff} vs. T for $\text{TiCl}_{1.70}(\text{i-OC}_4\text{H}_9)_{1.30}$.

○ ○ Experimental points;

— theoretical curve

($g = 1.95, J = -560 \text{ cm}^{-1}$).

Table 2

Values of parameters obtained on the basis of the Ising model

Compound	$\mu_{\text{eff}}/\text{B.M.}$	g	$-J/\text{cm}^{-1}$	$-J/J \cdot 10^{22}$
$\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$	1.57 (295 K)	1.89 (1.85)	25 (30)	5.0 (6.0)
$\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$	0.51 (291 K)	1.93	700	139.3
$\text{TiCl}_{1.86}(\text{OC}_2\text{H}_5)_{1.14}(\text{C}_2\text{H}_5\text{OH})_{0.35}$	0.50 (293 K)	1.94	750	149.2
$\text{TiCl}_{1.60}(\text{OC}_3\text{H}_7)_{1.40}$	0.64 (295 K)	1.92	490	97.5
$\text{TiCl}_{1.40}(\text{i-OC}_3\text{H}_7)_{1.60}$	0.63 (290 K)	1.92	520	103.5
$\text{TiCl}_{1.55}(\text{OC}_4\text{H}_9)_{1.45}$	0.59 (293 K)	1.95	580	115.4
$\text{TiCl}_{1.70}(\text{i-OC}_4\text{H}_9)_{1.30}$	0.59 (293 K)	1.95	560	111.4

In Fig. 8 the observed $\log [(4k/N\beta^2) \chi'_M T]$ is plotted against $1/T$ for the compound $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$ (the first step of thermal decomposition of complex $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$). The plot should be strictly linear except for the data at very low temperature. From the slope and the intercept of the straight line, the

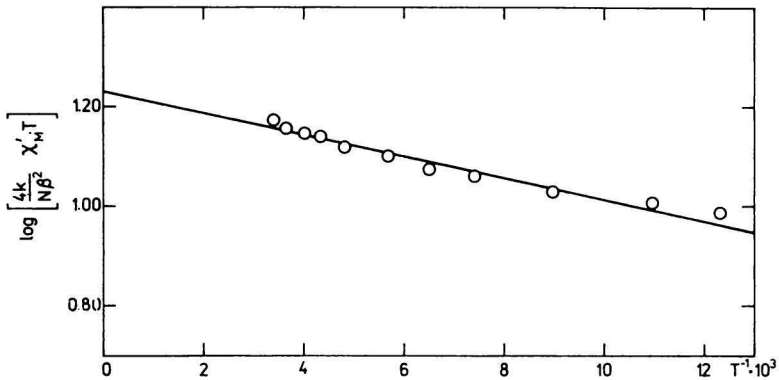


Fig. 8. $\log [(4k/N\beta^2) \chi'_m T]$ vs. $1/T$ for $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$.
 ○ ○ Experimental points ;
 — line calculated by the least square method from experimental data.

interaction energy and the g factor were evaluated as $J = -30 \text{ cm}^{-1}$ and $g = 1.85$, respectively (g factor from e.s.r. spectra was 1.89). For other studied compounds this evaluation failed, it probably depends on the magnitude of exchange interaction energy.

In our previous papers [5, 7] dealing with thermal properties of chloro-(aliphatic alcohol)titanium(III) complexes we have shown that the shapes of their decomposition curves differ from each other. This is assumed to depend on the crystal structure of parent complexes, which till now has been determined only for isopropyl alcoholic complex $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ [7, 18]. Though on the basis of electronic spectra and magnetochemical measurements [9] the same coordination number and distorted octahedral symmetry can be ascribed also to other parent complexes, the exact arrangement in their coordination sphere remains unknown.

According to observation in [5, 7] it may be assumed that the course of thermal decomposition and also the type of formed polymers are substantially influenced by the nature of coordination sphere in parent complex. From this point of view it is not possible to establish a relation between the value of the exchange interaction and the corresponding ligand on the basis of results presented in this work.

On the basis of relatively high values of exchange integrals of chloroalkoxotitanium(III) compounds, compared with the exchange integral of the complex with tetrahydrofuran, $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$ ($J = -185 \text{ cm}^{-1}$) [19], which is supposed to be a coordination polymer containing bridges $-\text{Ti}-\text{Cl}-\text{Ti}-$, it is possible to suggest simultaneous existence of $-\text{Ti}-\text{O}-\text{Ti}-$ bridges in the above compounds.

The assumption of successive formation of bridged structures and polymeric species is supported by the different values of exchange integrals in products from thermal decomposition of $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$. On the whole, a fairly good agreement

between theoretical curves and experimental data has been achieved. The numeric values of the exchange integrals are presented with accuracy up to tens of cm^{-1} . A higher precision would be beyond experimental possibilities especially at low temperature. In some cases also the determination of magnetic moment failed owing to its small value. For the same reason we neither took into account the possible temperature dependence of exchange integral which was found, e.g., for binuclear bis(cyclopentadienyl)titanium(III) bromide and iodide [20]. In the case of our compounds we do not exclude the possibility of its existence, though from our experimental results this dependence could not be established.

E.s.r. spectra were measured by G. Plesch.

References

1. Adams, R. W., Bishop, E., Martin, R. L., and Winter, G., *Aust. J. Chem.* **19**, 207 (1966).
2. Winter, G., *Inorg. Nucl. Chem. Lett.* **2**, 161 (1966).
3. Coutts, R. S. P., Martin, R. L., and Wailes, P. C., *Inorg. Nucl. Chem. Lett.* **9**, 981 (1973).
4. Gigenbach, W. and Brubaker, C. H., Jr., *Inorg. Chem.* **7**, 129 (1968).
5. Zikmund, M., Štepničková, L., and Hrnčiarová, K., *Chem. Zvesti* **22**, 917 (1968).
6. Zikmund, M., Štepničková, L., and Kohútová, M., *Chem. Zvesti* **23**, 856 (1969).
7. Zikmund, M., Hrnčiarová, K., Handlovič, M., and Brilla, M., *Chem. Zvesti* **33**, 206 (1979).
8. Zikmund, M., Valent, A., and Hrnčiarová, K., *Chem. Zvesti* **29**, 612 (1975).
9. Kohútová, M., *Chem. Zvesti* **33**, 187 (1979).
10. Figgis, B. N. and Martin, R. L., *J. Chem. Soc.* **1956**, 3837.
11. Martin, R. L. and Winter, G., *J. Chem. Soc.* **1965**, 4709.
12. Kyker, G. S. and Schram, A. P., *Inorg. Chem.* **8**, 2306 (1969).
13. Sinn, E., *Coord. Chem. Rev.* **5**, 313 (1970).
14. Dakternieks, D. R., Harris, C. M., Milham, P. J., Morris, B. S., and Sinn, E., *Inorg. Nucl. Chem. Lett.* **5**, 97 (1969).
15. Adams, R. W., Barraclough, C. G., Martin, R. L., and Winter, G., *Aust. J. Chem.* **20**, 2351 (1967).
16. Sinn, E., *Inorg. Nucl. Chem. Lett.* **5**, 193 (1969).
17. Inoue, M., Emori, S., and Kubo, M., *Inorg. Chem.* **7**, 1427 (1968).
18. Handlovič, M. and Hanic, F., *J. Cryst. Mol. Struct.* **4**, 327 (1974).
19. Zikmund, M., Kohútová, M., Handlovič, M., and Mikloš, D., *Chem. Zvesti* **33**, 180 (1979).
20. Coutts, R. S. P., Martin, R. L., and Wailes, P. C., *Aust. J. Chem.* **26**, 47 (1973).

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