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Ditertiary Phosphine Oxides Complexes with Ni^{II} and Co^{II} Halides

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New coordination compounds containing the ligands bis(diphenylphosphine oxide)methane (DPMO), 1,2-bis(diphenylphosphine oxide)ethane (DPEO), and 1,3-bis(diphenylphosphine oxide) propane (DPPO) are reported. On the basis of analytical data, infrared and electronic spectra, magnetic, conductivity and molecular weight measurements the complexes are formulated $[M(DPMO)_3][MX_4]$ *(M = Co, Ni; X = Cl, Br, I),* $[Ni(DPEO)_3][NiX_4]$ *with a tetrahedral structure in the anionic species and a probably octahedral structure in the cationic species, and* $[M(DPPO)X_2]$ *(M = Co, Ni) and* $[Co(DPEO)X_2]$ *with a pseudotetrahedral structure.*

Introduction

Complexes of 3d metal ions with triphenylphosphine- and arsine oxide have been extensively studied by a number of authors in the recent years.[1] However a little attention has been payed to ditertiary phosphine oxides as ligands. Therefore it seemed us interesting to study the coordinating properties of the ligands: bis(diphenylphosphine oxide)methane (DPMO), 1,2-bis(diphenylphosphine oxide)ethane (DPEO), and 1,3-bis(diphenylphosphine oxide)propane (DPPO), towards Ni^{II} and Co^{II} halides. To our knowledge only the complexes with Cu^{II} Sn^{IV} Zr^{IV} and U^{VI} have been prepared with these ligands. [2,3]

Experimental Section

Synthesis of the Ligands and Complexes. The ligands were prepared by oxidation of the appropriate ditertiary phosphines dissolved in acetone with a 30% hydrogen peroxide solution.[4]

The complexes were prepared using the same general procedure: a solution of 2 mmoles of the anhydrous metal halide in 20 ml of boiling butan-1-ol was added to the stoicheiometric amount of the appropriate ligand in 10 ml of the same solvent. In some cases the solutions were concentrated and cyclohexane added until crystallization began. The crystalline products were filtered and dried *in vacuo* at 70°C.

Physical Measurements. All physical measurements were carried out as previously described;[5] the solutions used for molecular weight, conductivity and spectral measurements were *ca.* 5.10^{-4} *M*. Analytical and some physical data are reported in Table I.

Results and Discussion

Complexes with the Ligand DPMO. Co^{II} and Ni^{II} halides give rise to crystalline adducts with the ligand DPMO having general formula $2MX_2 . 3DPMO$. The average magnetic moments values *per* metal ion (Table I) are in the usual range for high spin Co^{II} and Ni^{II} complexes. The electronic spectra, both in the solid state and in nitroethane solution, were all recorded and the maxima positions reported in Table II. The reflectance spectra of the Ni^{II} complexes in the range 7-20 kK as well as those of Co^{II} complexes in the range 5-15 kK are quite similar to those well known of the corresponding tetrahedral tetrahalometallates[6] (Figure 1). The infrared spectra show metal-halogen stretching vibrations in the range 200-300 cm^{-1} (Table III) which are diagnostic for the MX_4^{2-} species.[5a] Spectroscopic evidencies and analytical data lead to formulate the complexes as $[M(DPMO)_3][MX_4]$. Regarding the stereochemistry of the $[M(DPMO)_3]^{2+}$ cations, the coordination trough the phosphoryl oxygen is clearly shown by the P—O stretching frequencies which are shifted towards the low energy region upon coordination[7] (Table III).

The reflectance spectrum of the compound $[Ni(DPMO)_3][NiCl_4]$ shows a weak d—d band at 23.5 kK in addition to the bands of the $NiCl_4^{2-}$ ion (Table II). The spectrum of the complex $[Ni(DPMO)_3][ZnCl_4]$, which has been found by X-ray powder pattern to be isomorphous with the nickel complex, shows

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(1) L.M. Venanzi, *J. Chem. Soc.*, 719 (1958); F.A. Cotton and D.M.L. Goodgame, *J. Amer. Chem. Soc.*, *82*, 5771 (1960); B.N. Figgis, J. Lewis, F. Mabbs, and G.A. Webb, *J. Chem. Soc.*, 1411 (1966); F. Mani, *Inorg. Nucl. Chem. Letters*, 7, 447 (1971) and references therein.

(2) (a) M. Mathew and G.J. Palemik, *Canad. J. of. Chem.*, *47*, 1963 (1969); (b) Z.A. Sheka, K.B. Yatsimirskii, and M.A. Ablova, *Zhurn. Neorg. Khim.*, *15*, 2932 (1970).

(3) S.S. Sandhu and S.S. Sandhu, *J. Inorg. Nucl. Chem.*, *31*, 1363 (1969); G.P. Nikitina and M.F. Pushlenkov, *Radiokhimiya*, 5, 456 (1963); S.S. Sandhu, *Chem. Ind.* (*London*), 33, 1405 (1967).

(4) W. Hewertson and H.R. Watson, *J. Chem. Soc.*, 1490 (1962); R.L. Shriner and C.N. Wolf, *Org. Synth.*, *30*, 97 (1950).

(5) (a) A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, *86*, 17 (1964); (b) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 6, 262 (1967); *ibidem*, 7, 1417 (1968).

(6) N.S. Gill and R.S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(7) F.A. Cotton, R.D. Barnes, and E. Bannister, *J. Chem. Soc*, 2199 (1960).

Table I. Analytical and some physical data for the complexes

Compound	Molar conductance $cm^2ohm^{-1}M^{1-}$ [a]	i [b]	C% Calcd	C% Found	H% Calcd	H% Found	Metal% Calcd	Metal% Found	μ_{eff},B.M.(°K) [c]
$[Ni(DPMO)_3][ZnCl_4]$			59.43	59.00	4.38	4.67			3.41(298)
$[Ni(DPMO)_3][NiCl_4]$	87		59.75	59.71	4.44	4.60	7.79	7.80	3.62(297)
$[Ni(DPMO)_3][NiBr_4]$	109		53.41	53.53	3.94	4.25	6.97	6.80	3.56(297)
$[Ni(DPMO)_3][NiI_4]$	104		48.04	48.31	3.54	3.85	6.27	5.71	3.30(300)
$[Co(DPMO)_3][CoCl_4]$	74		59.73	60.17	4.44	4.87	7.82	7.68	4.87(300)
$[Co(DPMO)_3][CoBr_4]$	86		53.43	52.98	3.94	4.27	6.99	6.84	4.86(295)
$[Co(DPMO)_3][CoI_4]$	95		48.03	48.39	3.54	3.88	6.29	6.19	5.00(295)
$[Ni(DPEO)_3][NiCl_4]$	49		60.42	60.83	4.69	4.75	7.57	7.64	3.75(293)
$[Ni(DPEO)_3][NiBr_4]$	93		54.21	54.20	4.21	4.05	6.79	6.93	3.62(293)
$[Ni(DPEO)_3][NiI_4]$	142		48.88	49.16	3.80	3.83	6.13	6.23	3.47(293)
$[Co(DPEO)Cl_2]$	26		55.70	55.69	4.32	4.40	10.52	10.74	4.70(293)
$[Co(DPEO)Br_2]$	23		48.10	48.55	3.73	3.84	9.08	9.22	4.71(293)
$[Co(DPEO)I_2]$	29		42.02	42.51	3.25	3.50	7.94	7.71	4.74(293)
$[Ni(DPPO)Br_2]$	24	0.74	48.91	48.91	3.96	4.13	8.84	8.54	3.68(300)
$[Ni(DPPO)I_2]$	55	0.89	42.84	42.71	3.46	3.72	7.76	7.76	3.76(300)
$[Co(DPPO)Cl_2]$	5	0.96	56.47	56.60	4.56	4.89	10.26	10.23	4.65(300)
$[Co(DPPO)Br_2]$	4	0.78	48.90	49.44	3.96	4.35	8.86	8.45	4.70(300)
$[Co(DPPO)I_2]$	16	0.88	42.83	42.00	3.46	3.44	7.78	7.24	4.73(300)

[a] For *ca.* 5×10^{-4} *M* solutions in nitroethane at 298°K. [b] Van't Hoff coefficients for *ca.* 5×10^{-4} *M* solutions in nitroethane at 310°K. [c] Average magnetic moment values calculated *per* metal ion.

Table II. Spectrophotometric data for the complexes.

Compound	State [a]	Absorption max., kK(ε_{molar} for solution.)
$[Ni(DPMO)_3][ZnCl_4]$	R	7.2; 12.3; 14.5sh; 20.6sh; 23.5.
$[Ni(DPMO)_3][NiCl_4]$	R	7.4; 15.0; 20.8sh; 23.6.
	N	8.7(34); 14.3(100); 15.3(115); 16.7(95); 18.2sh; 23.7(40).
$[Ni(DPMO)_3][NiBr_4]$	R	6.9; 14.0; 18.3; 23sh.
	N	8.4(45); 13.3(95); 14.3(130); 15.9(140); 16.7sh.
$[Ni(DPMO)_3][NiI_4]$	R	6.9; 11,7; 18.9sh; 20.0.
	N	8.3(30); 14.6(105); 19.0(670).
$[Co(DPMO)_3][CoCl_4]$	R	5.5; 6.1; 15.2; 15.7sh; 18.5.
	N	6.2(100); 7.5(130); 15.0(440); 15.9sh; 17.2(230).
$[Co(DPMO)_3][CoBr_4]$	R	5.6; 8.3; 14.5; 18.4.
	N	5.5(57); 7.4(62); 13.9sh; 14.4(650); 15.5(515); 16.4(270); 18.5sh.
$[Co(DPMO)_3][CoI_4]$	R	5.0; 13.2; 13.7sh; 18.2
	N	8(5); 17.8(72); 20sh.
$[Ni(DPEO)_3][NiCl_4]$	R	7.3; 14.8; 20.0sh; 23.3.
	N	8.5(30); 14.2sh; 15.0(85); 16.7(100); 18sh; 23.5sh.
$[Ni(DPEO)_3][NiBr_4]$	R	7.0; 10.5sh; 13.7; 18.2; 23.5.
	N	8.6(50); 14.3sh; 16.1(180); 16.8sh.
$[Ni(DPEO)_3][NiI_4]$	R	7.0; 11.8; 18.8sh; 19.6.
	N	8.5(50); 14.7(120); 18.9(725).
$[Co(DPEO)Cl_2]$	R	5.8; 6.8; 15.0; 16.7.
	N	5.9(40); 6.9(38); 15.1(490); 17.1(245).
$[Co(DPEO)Br_2]$	R	5.7; 6.4; 15.0; 16.0sh.
	N	5.7(34); 6.9(50); 14.7(380); 16.2(310).
$[Co(DPEO)I_2]$	R	5.5; 6.3; 14.2; 15.4.
	N	5.7(78); 6.6(88); 13.8(390); 14.7(330); 16.0sh.
$[Ni(DPPO)Br_2]$	R	7.1; 8.0sh; 14.8sh; 16.0; 21.0; 24.1.
	N	8.5(25); 14.3sh; 16.0(100); 16.8sh; 21.0(25).
$[Ni(DPPO)I_2]$	R	7.2; 13.5sh; 15.4; 18.7; 22.0.
	N	8.3(17); 13.5sh; 14.5(83); 18.7(350).
$[Co(DPPO)Cl_2]$	R	5.7; 6.8; 8.5sh; 15.4; 16.1sh; 19.2.
	N	5.7(47); 6.9(40); 9.0sh; 15.0(400); 15.4sh; 17.0(235); 19.0sh.
$[Co(DPPO)Br_2]$	R	5.6; 6.6; 15.3; 16.0sh; 19.3.
	N	5.6(52); 6.8(47); 14.8(410); 15.5(375); 16.4(284).
$[Co(DPPO)I_2]$	R	5.5; 6.3; 14.5; 15.9sh; 19.6.
	N	5.4(56); 6.4(62); 13.9(370); 14.8(400); 15.4sh; 16.1(290).

[a] R = Diffuse Reflectance; N = Nitroethane.

three more intense bands at 7.2, 13.2, and 23.5 kK and two shoulders at *ca.* 15.0 and 20.0 kK (Figure 1). On the basis of these electronic spectra alone, it is troubly to assign a six-coordinate or a five-coordinate stereochemistry to these cationic species.[8] However on account of the bidentate nature of the ligand and the lack of the free P=O stretching frequency in the i.r. spectra of these complexes, we feel that the present $Ni(DPMO)_3^{2+}$ complex is six-

(8) F.A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, *82*, 2986 (1960); N.M. Karayannis, E.E. Broadshow, L.L. Pytlewski, and M.M. Labes, *J. Inorg. Nucl. Chem.*, *32*, 1079 (1970) and references therein; N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski, and M.M. Labes, *Inorg. Chim. Acta*, *4*, 557 (1970) and references therein.

Table III. Infrared data for the complexes (frequencies in cm^{-1}).

Compound	ν(P–O)	ν(M–X)^a
DPMO	1192	
$[Ni(DPMO)_3][NiCl_4]$	1165	285
$[Ni(DPMO)_3][NiBr_4]$	1165	220
$[Ni(DPMO)_3][NiI_4]$	1165	197 sh, 190
$[Co(DPMO)_3][CoCl_4]$	1165	295
$[Co(DPMO)_3][CoBr_4]$	1165	232sh, 222
$[Co(DPMO)_3][CoI_4]$	1165	198sh, 192
DPEO	1185	
$[Ni(DPEO)_3][NiCl_4]$	1150	285
$[Ni(DPEO)_3][NiBr_4]$	1150	228
$[Ni(DPEO)_3][NiI_4]$	1150	193
$[Co(DPEO)Cl_2]$	1150	
$[Co(DPEO)Br_2]$	1150	
$[Co(DPEO)I_2]$	1145	
DPPO	1185	
$[Ni(DPPO)Cl_2]$	1155	
$[Ni(DPPO)Br_2]$	1155	
$[Ni(DPPO)I_2]$	1148	
$[Co(DPPO)Cl_2]$	1150	
$[Co(DPPO)Br_2]$	1150	
$[Co(DPPO)I_2]$	1140	

^{a} For MX_4^{2-} species.

coordinate. Moreover the $[Co(DPMO)_3][CoCl_4]$ complex, which is isomorphous with the analogous Ni^{II} derivative, shows a band at 18,5 kK in the reflectance spectrum which is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of the CoO_6 chromophore.

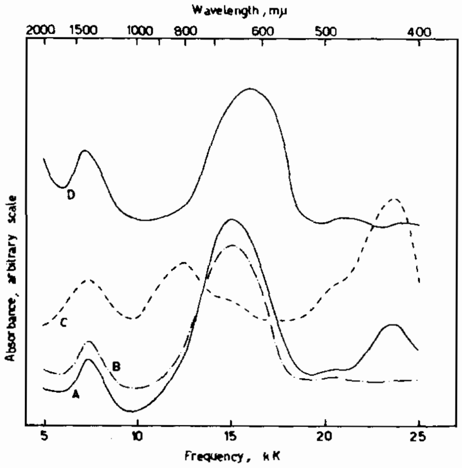

Figure 1. Reflectance spectra of: $[Ni(DPMO)_3][NiCl_4]$, curve A; $[Et_4N]_2[NiCl_4]$, curve B; $[Ni(DPMO)_3][ZnCl_4]$, curve C; $[Ni(DPPO)Br_2]$, curve D.

Behaviour in Solution. These complexes are not soluble in the common non coordinating solvents e.g. C_6H_6, $CHCl_3$, $ClCH_2CH_2Cl$ although they are slightly soluble in nitroethane and quite soluble in methyl and ethyl alcohol where extensive solvolysis is observed through a marked change in color of the solutions. The low solubility of these complexes is consistent with the ionic formula assigned to the compounds. The absorption spectra of the Co^{II} and Ni^{II} complexes in nitroethane solution differ to some extent from those in the solid state and essentially show the bands of the solvolysed tetrahedral MX_4^{2-} species.[9] Conductivity values (Table I) and electronic spectra indicate that the nickel complexes are solvolysed to a larger extent than the cobalt complexes.

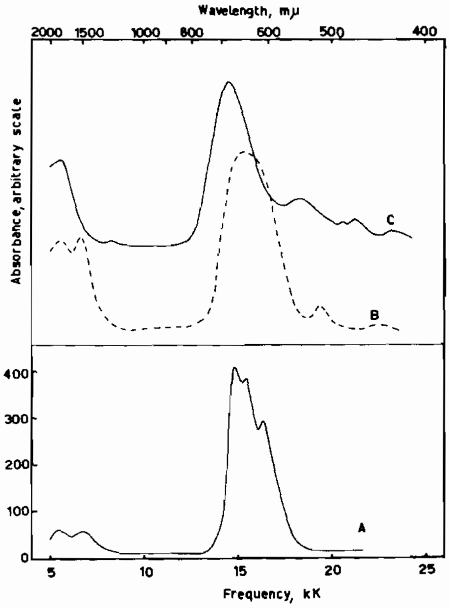

Figure 2. Absorption spectrum of $[Co(DPPO)Br_2]$ in nitroethane, curve A; reflectance spectra of: $[Co(DPPO)Br_2]$, curve B; $[Co(DPMO)_3][CoBr_4]$, curve C.

Complexes with the Ligand DPPO. The DPPO ligand forms high spin complexes with Ni^{II} and Co^{II} halides having the general formula $M(DPPO)X_2$ (X = Cl, Br, I; M = Ni, Co). The reflectance spectra which are quite similar to the solution spectra in nitroethane (Table II; Figures 1 and 2) correlate very closely to those of the pseudo-tetrahedral ML_2X_2 (L = Ph_3PO, Ph_3AsO) both in the shape and frequencies of the bands.[1,10] Also the magnetic moment values are typical of this type of complexes. The present Ni^{II} and Co^{II} complexes are almost insoluble in the common non coordinating organic solvents with the exception of nitroethane where the complexes dissolve slowly even at the boiling temperature. Molecular weight and conductivity measurements (Table I) lead to the conclusion that these complexes are non ionic and monomeric in solution. However their low solubility when compared to the large solubility of the $M(Ph_3PO)_2X_2$ complexes seems to support the hypothesis of a polymeric pseudo- tetrahedral structure in the solid state with a ligand molecule bridging two metal ions. Such a possibility was proposed for the adducts of $Ph_2P(CH_2)_nPPh_2$ ligands (n = 4,5) with Ni^{II} and Co^{II} halides.[11] Moreover a X-ray structure has shown a polymeric pseudo-tetrahedral coordination for the $Cu(DPEO)Cl_2$ complex.[2a]

(9) Absorption spectra of the complexes $[Et_4N]_2[MX_4]$ (M = Co, Ni; X = Cl, Br, I) in $5.10^{-4}M$ nitroethane solution have been recorded for comparision purposes.

(10) D.J. Phillips and S.Y. Tyree, Jr., *J. Amer. Chem. Soc.*, *83*, 1806 (1961); D.M.L. Goodgame, M. Goodgame, and F.A. Cotton, *Inorg. Chem.*, *1*, 239 (1962).

(11) L. Sacconi and J. Gelsomini, *Inorg. Chem.*, *7*, 291 (1968).

Complexes with the Ligand DPEO. Analogously to the complexes with the ligand DPMO, complexes of general formula 2NiX$_2$. 3DPEO were obtained with the ligand DPEO and Ni^{II} halides. Again the complexes have been formulated [Ni(DPEO)$_3$][NiX$_4$] from spectral evidencies both in the solid state and in solution (Table II). The cobalt complexes, on the contrary, have been obtained with the general formula Co(DPEO)X$_2$, their spectra and magnetic moment values being quite similar to those of the DPPO cobalt complexes. Therefore an analogous non ionic [Co(DPEO)X$_2$] formula and a pseudo-tetrahedral structure has to be assigned to these complexes.

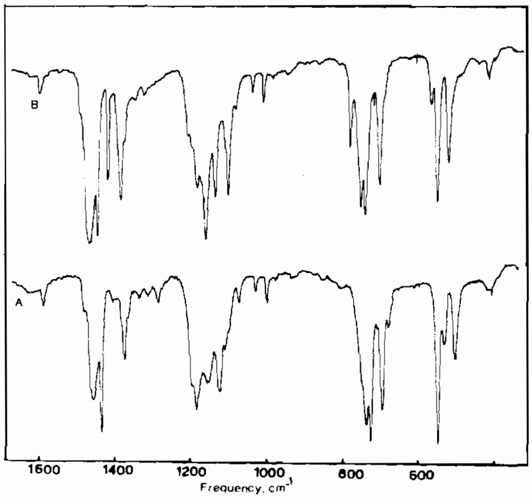

Figure 3. Infrared spectra of: [Ni(DPEO)$_3$][NiBr$_4$], curve A; and [Co(DPEO)Br$_2$], curve B.

The infrared spectra of the [Co(DPEO)X$_2$] and [Ni(DPEO)$_3$][NiX$_4$] complexes show a set of vibrational bands attributable to the (C$_6$H$_5$)$_2$P(O)-group[12,13] which are identical for the two types of complexes. However a marked change is observed in the range of CH$_2$ deformations.[14] In particular the spectra of the Co^{II} complexes show three strong bands (Figure 3) at *ca.* 1400, 1090, 770 cm^{-1} (probably assigned to the δCH$_2$, τCH$_2$, ρCH$_2$ respectively) which are not present in the Ni^{II} complexes. These bands are also shown by the Cu(DPEO)Cl$_2$ complex which has been shown to have a polymeric structure with bridging DPEO ligand. It is therefore reasonable to assume that the different conformation of the ligand in the Ni^{II} and Co^{II} complexes is responsable for the observed differencies in the i.r. spectra. This is consistent with the features of the infrared spectra of the *trans* and *gauche* rotational isomers of 1,2-ethane disostituted derivatives[15]. On this basis a *trans* bridging conformation is assigned to the DPEO ligand in the cobalt complexes, whereas a chelate conformation distorted towards the *gauche* form is assigned to the DPEO ligand in the nickel complexes.

Conclusion

These results show that the behaviour of the ligands reported here depends both on the steric requirements of the ligands and on the electronic properties of the metal ions. The DPMO ligand which can form six-membered chelate rings give rise to six-coordinate complexes with a metal to ligand ratio 1:3. It is been shown that six-membered chelate rings involving two double bonds are quite stable[16].

The DPPO ligand give rise to 1:1 complexes with a tetrahedral stereochemistry. The structure of these complexes might be poly meric for analogy with the DPEO cobalt complexes, on account of their low solubility and in view of the low stability of eight-membered chelate rings. It is well established that the increasing length of the chain diminishes the chelate effect and the tendency to form polymeric structures is increased[16,17].

The DPEO ligand which forms 1:1 tetrahedral complexes with Co^{II} and 1:3 six-coordinate Ni^{II} cations, seems to have a critical size for which electronic factors of the metal became more important of the steric requirements of the ligands in determing the stereochemistry of these complexes.

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(12) In order to identify the P=O stretching frequency for the DPEO complexes, their i.r. spectra were compared with those of triphenylphosphine-oxide and DPEO-d$_4$ Ni^{II} and Co^{II} complexes (DPEO-d$_4$=Ph$_2$P(O)CD$_2$CD$_2$P(O)Ph$_2$). On this basis the bands at 1190 and 1175 cm^{-1} in the i.r. spectra of DPEO Ni^{II} and Co^{II} complexes are assigned to the CH$_2$ wagging mode and to an in-plane CH deformation of the phenyl group, respectively.

(13) G.B. Deacon and J.H.S. Green, *Spectrochim. Acta, 24A*, 845 (1968).

(14) W. Sawodny, K. Niedenzu, and J.W. Dawson, *Spectrochim. Acta, 23A*, 799 (1967) and references therein.

(15) S. Mizushima, I. Ichishima, I. Nakagawa, and J.V. Quagliano, *J. Phys. Chem.*, 59, 293 (1955) and references therein.

(16) R.W. Parry, The Chemistry of the Coordination Compounds, ed. J.C. Bailar, Jr., Reinhold Publishing Corporation, New York, 1956, p. 220.

(17) Jørgensen, Inorganic Complexes, Academic Press, London, 1963, p. 66, and references therein.