# 46. Molecular Structure of the Bis[tris(2-aminoethyl)aminecyano]dicobalt(III) Ion and its UV/VIS Spectrum

by **Silvio Fallab*** and **Margareta Zehnder**

Institut für Anorganische Chemie der Universität Basel, Spitalstr. 51, CH-4056 Basel

Dedicated to Prof. *J. D. Dunitz* on the occasion of his 60th birthday

(6.IX.83)

## *Summary*

Formation of μ-peroxodicobalt(III) complexes has been studied in solutions containing tris(2-aminoethyl)aminecobalt(II) and additional monodentate ligands X. Depending on the nature and the concentration of X and on pH, singly bridged $[(tren)XCoOOCoX(tren)]^{4+}$ and/or doubly bridged $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ are formed. The UV/VIS spectra of these complexes are discussed on the basis of a theoretical model which stresses the importance of the dihedral angle of the CoOOCo-group. $[(tren)(CN)CoOOCo(CN)(tren)](ClO_4)_2$ has been synthesized and its structure determined by single crystal X-ray diffraction. The CoOOCo-group of the cation is planar. Solutions of the complex as well as the solid show two CT bands in the 300–400 nm region.

Oxygenation of Co(II)-complexes invariably leads to products which strongly absorb in the near UV. Their absorption spectrum is characterized by broad and intense CT bands reaching into the visible and thus giving rise to yellow and brown solution colors [1]. Somewhat conflicting rules relating the number of bands observed between 250 and 450 nm to the structure have been published in [2–4]. Empirically, three types of spectra can be distinguished *(Fig. 1)*: *i.* Most common in singly bridged μ-peroxodicobalt(III) complexes $L_5CoOOCoL_5$ is a strong band close to 300 nm with a molar extinction $\varepsilon \geqslant 10000 M^{-1}\ cm^{-1}$. In addition, a flat shoulder of much lower intensity around 400 nm is frequently observed. *ii.* In some cases the main absorption band seems split into two peaks of lower but approximately equal intensity with maxima

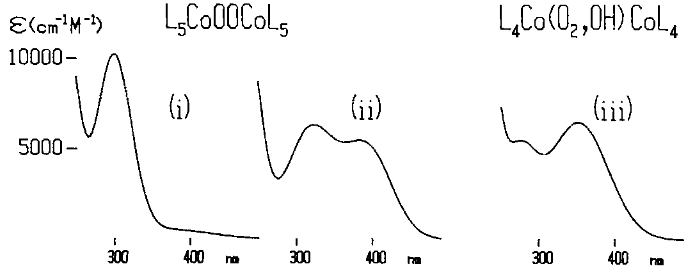

Fig. 1. *Types of UV/VIS spectra shown by singly and doubly bridged μ-peroxodicobalt(III) complexes*

between 300 and 400 nm. *iii.* A two-band spectrum is also observed with complexes of the doubly bridged type $L_4Co(O_2,OH)CoL_4$ in which the additional bridging ligand forces the CoOOCo-group into a *cisoid*-nonplanar arrangement with a dihedral angle close to 60° [5] [6]. In this case, however, the high energy band is well below 300 nm.

Attempts to explain these differences in relation to structure have not been satisfactory so far [4]. To obtain further information regarding singly bridged μ-peroxo complexes we studied dioxygen uptake in dilute solutions containing the tris(2-aminoethyl)aminecobalt(II) ion[1]) and additional monodentate ligands X. This system is ideally suited for a more systematic comparison of spectra because oxygenation of $Co(tren)^{2+}$ leads to one isomer only [6]. With $X = NH_3$ a singly bridged bis(ammine)-complex is formed, the structure of which has been determined [7]. Like many other μ-peroxodicobalt(III) ions with five N-donor groups at each metal centre, it has a *transoid*-planar CoOOCo-group and a type *i* spectrum. At low $[NH_3]$ a mixture of $[(tren)(NH_3)CoOOCo(NH_3)(tren)]^{4+}$ and $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ is obtained. The observed absorption can then be explained by superposing type *i* and type *iii* spectrum, and the concentration ratio of the two products depends only on $[NH_3]$ and pH.

Similar results are obtained with $X = RNH_2$ ($R = CH_3$, $C_2H_5$, $C_3H_7$). But owing to steric crowding a much higher concentration of these ligands is needed to shift the equilibrium towards the singly bridged bis($RNH_2$)-complex. With $X = (CH_3)_2NH$ steric crowding obviously prevents coordination since solutions containing the secondary amine in concentrations up to 1 M show the unperturbed spectrum *iii.*

Two classes of spectra are found when using charged ligands X such as $CN^-$, $HPO_4^{2-}$, $NO_2^-$, $SCN^-$, $OCN^-$ of $N_3^-$. While the first three lead to μ-peroxo complexes with a type *ii* absorption, in the presence of $SCN^-$, $OCN^-$ and $N_3^-$ oxygenation of $Co(tren)^{2+}$ produces spectra resembling type *iii*. Since these anions have been shown to function as bridging ligands [8–10] the corresponding oxygenation products may well be of the doubly bridged type. Type *ii* spectra have been observed before with various ligands, *e.g.* $(his)_2CoOOCo(his)_2$ [11], but no structural information is available so far which would allow a possible correlation between molecular geometry and UV/VIS absorption. We therefore attempted an X-ray crystallographic investigation on μ-peroxodicobalt(III) complexes with type *ii* spectrum. In this communication, we report on the structure of $[(tren)(CN)CoOOCo(CN)(tren)]^{2+}$.

**Experimental.** – Crystals for X-ray analysis of the title compound were obtained by adding 1.50 g solid $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4$[12] to 50 ml of an aq. solution containing 0.97 g tren (free base) and 0.52 g KCN; the ratio Co/tren/CN was 1:1,25:1.5. After vigorous stirring for 30 min to remove $NH_3$, a 2-fold excess of $NaClO_4 \cdot H_2O$ was added to the filtered solution; it was then set aside in an ice bath and gave blackbrown crystals after 1–2 h.

*Crystal Data.* $[(tren)(CN)CoOOCo(CN)(tren)](ClO_4)_2$, $C_{14}H_{36}Cl_2Co_2N_{10}O_{10}$, monoclinic, $a = 21.024(6)$, $b = 8.061(2)$, $c = 16.245(4)$, $\beta = 95.46(3)°$, $Z = 4$, space group $C2/c$ or $Cc$[2]).

---

[1]) Abbreviated as $Co(tren)^{2+}$.

[2]) The systematic absences indicate the monoclinic space group $C2/c$ or $Cc$. E-statistics, computed as a function of sin $\theta/\lambda$ did not permit a clear distinction between the centric and the noncentric space group. Assuming the centric case the CoOOCo-unit of the binuclear cation is required to be planar. Although refinements were successful with space group $C2/c$, this does not *a priori* exclude the non-centric case, where the cation would have a pseudo-symmetric structure. Least-squares refinements carried out separately with both space groups lead to comparable bond distances, bond angles, thermal parameters and *R*-indices.

Intensity data were collected with Mo$K_\alpha$ radiation out to $\theta = 27°$ ($\theta$–$2\theta$ scan mode). Unit cell parameters were obtained from accurate centering of 25 strong independent reflexions. Intensities of 1736 independent reflections were measured with an *Enraf-Nonius CAD4* diffractometer equipped with a graphite monochromator. No absorption correction was applied ($\mu_{Mo} = 2.9$ cm$^{-1}$).

*Solution and Refinement of the Structure.* The position of the Co-atom was determined by direct methods using the program *Multan-80* [13]. A weighted difference *Fourier* map followed by least-squares refinements and further difference *Fourier* maps located the remaining atoms. Positions of protons were not considered. All 1736 reflections were used in the anisotropic refinement with unit weights; the final $R$-index was 0.08. Programs used were developed partly by *G. M. Sheldrick* [14] and partly by ourselves. Scattering factors for $Co^{3+}$ and neutral atoms and terms for anomalous dispersion were those of *Cromer et al.* [15] [16]. The perchlorate anion is disordered, two of the O-atoms being split into half-populated positions. Atomic positional and thermal parameters are sent to the *Cambridge Data Base* or are available from *M.Z. Fig. 2* shows the ORTEP plot, and the *Table* gives relevant interatomic distances and selected bond angles of the cation.

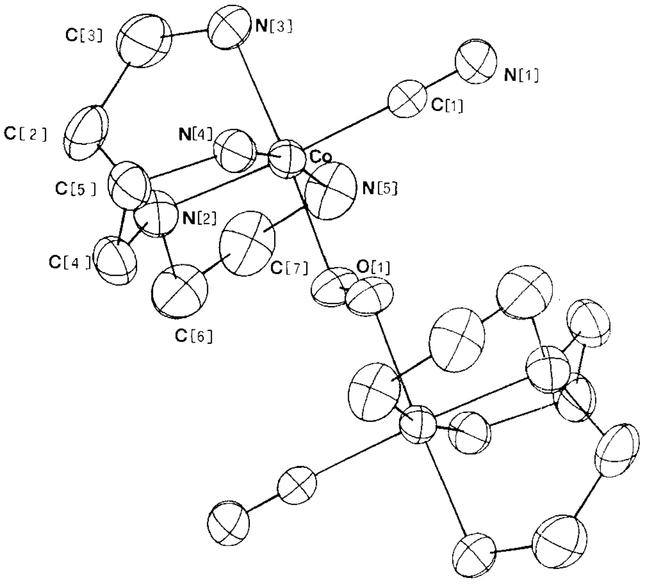

Fig. 2. *ORTEP drawing of the cation [(tren)(CN)CoOOCo(CN)(tren)]*$^{2+}$

*Reactivity Studies.* The solution behaviour of the complex has been studied only in a preliminary way [17]. Dissolved in $H_2O$ or in a weakly basic buffer it is stable for hours. In weakly acidic solution of pH > 3 it decomposes mainly (70%) to Co(II)-complex and $O_2$. The reactivity changes drastically with increasing acidity: At pH 2 less than 20% of Co(II) can be recovered and the final spectrum points to mononuclear Co(III)-fragments which have not been identified. When studying the acidification on a shorter time scale a spectral change is observed which suggests a fast protonation of the complex ion. Spectra were recorded with a diode array spectrophotometer *Hewlett-Packard 8450*.

**Discussion.** – As in most of the singly bridged μ-peroxodicobalt(III) complexes investigated so far, the midpoint of μ-$O_2$ in $[(tren)(CN)CoOOCo(CN)(tren)]^{2+}$ coincides with a centre of symmetry of the unit cell[3]).

The angle CoOO (*ca.* 113°) is in accordance with the previously reported values [7] for singly bridged μ-peroxo complexes. For the other bond angles no significant distor-

---

[3]) An exception has been found recently [18] in $[(bag)(NH_3)CoOOCo(NH_3)(bag)]^{2+}$ (bag = bis(2-aminoethyl)glycine).

Table. *Selected Bond Distances and Bond Angles in the Cation and their Standard Deviations*

| Atoms | Distance [Å] | Atoms | Angle [°] |
|---|---|---|---|
| Co–O(1) | 1.899(6) | C(1)–Co–O(1) | 92.2(3) |
| Co–N(2) | 1.991(8) | N(2)–Co–O(1) | 90.9(3) |
| Co–N(3) | 1.998(7) | N(2)–Co–C(1) | 176.0(3) |
| Co–N(4) | 1.949(7) | N(3)–Co–O(1) | 176.6(3) |
| Co–N(5) | 1.987(8) | N(3)–Co–C(1) | 91.1(3) |
| Co–C(1) | 1.912(10) | N(3)–Co–N(2) | 85.9(3) |
| O(1)–O(1') | 1.494(11) | N(4)–Co–O(1) | 88.0(3) |
| C(1)–N(1) | 1.129(12) | N(4)–Co–C(1) | 91.1(4) |
| | | N(4)–Co–N(2) | 86.5(3) |
| | | N(4)–Co–N(3) | 93.0(3) |
| | | N(5)–Co–O(1) | 84.8(3) |
| | | N(5)–Co–C(1) | 95.9(4) |
| | | N(5)–Co–N(2) | 86.9(3) |
| | | N(5)–Co–N(3) | 93.9(3) |
| | | N(5)–Co–N(4) | 170.1(3) |
| | | Co–O(1)–O(1') | 113.4(10) |

tion of the octahedral geometry is observed. The two Co–C bond lengths determined (1.857 and 1.941 Å) are quite normal for cyanocobalt(III) species [19]. In $[(CN)_5CoOOCo(CN)_4]^{6-}$ values betwen 1.874 and 1.912 Å were found [20]. Co–N distances vary from 1.938 to 2.028 Å. No significant difference between positions *cis* and *trans* to the bridging ligand can be detected.

A simple MO model proposed by *Miskowski et al.* [21] and elaborated further by *Lever & Gray* [4] accounts in principal for the observed intense UV/VIS absorption of μ-peroxodicobalt(III) complexes. Since the bridging ligand always has a O–O distance close to 1.48 Å it may be assumed to have the electronic structure of a peroxide group with filled $\pi^*$-orbitals perturbed by interaction with two $Co^{III}$-centres. This picture is consistent with O–O stretching frequencies observed by *Raman* spectroscopy resembling those in $H_2O_2$ and $Na_2O_2$ [22]. An alternate viewpoint which stresses the spin-pairing aspect of the $O_2$-addition reaction has been taken by *Drago & Corden* [23]. Combining the radicals $Co^{II}$ and $O_2$ will of course lead to a similar orbital description of the binuclear complex, but its equilibrium ground-state geometry is obviously better approximated by assuming donation of an electron pair from $O_2^{2-}$ to $Co^{III}$.

There is a general agreement about the bonds formed in the $O_2$-addition reaction as being due to overlap between $\pi^*(O_2^{2-})$ and $d_{z^2}$ (Co) [24] *(Fig. 3a)*. In a planar CoOOCo-unit as found in many singly bridged μ-peroxo complexes [7] the two filled $\pi^*$-orbitals of the bridging group will be split into a strongly bonding $\pi_h^*$ *(Fig. 3a)* and a $\pi_v^*$ which is perpendicular to the plane of the molecular framework and will therefore be weakly $\pi$-bonding. On this basis the UV/VIS absorption of $(CN)_5CoOOCo(CN)_5^{6-}$ has been explained [21]. The spectrum is governed by an intense band at 315 nm due to the $\sigma \rightarrow \sigma^*$ transition *(Fig. 3b)*. While in this case the $\pi_v^* \rightarrow d_\sigma^*$ transition shows a pronounced shoulder at 370 nm, in other singly briged complexes namely $(NH_3)_5CoOOCo(NH_3)_5^{4+}$, $(tren)(NH_3)CoOOCo(NH_3)(tren)^{4+}$ and (dien)-$(NH_3)_2CoOOCo(NH_3)_2(dien)^{4+}$, it may be obscured by a broader 'in-plane' charge-transfer band [21] resulting in a type *i* spectrum *(cf. Fig. 1)*.

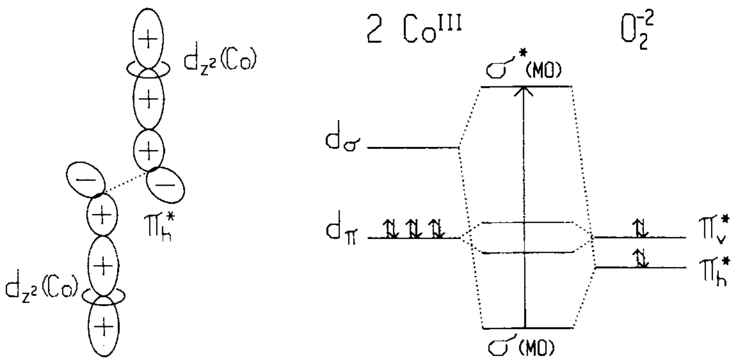

Fig. 3. (a) *Schematic orbital description of bonding in singly bridged μ-peroxodicobalt(III) complexes with a* transoid-*CoOOCo-group;* (b) *qualitative representation of the energy levels of the interacting orbitals*

Spectra of type *i* are also exhibited by (dien)(en)CoOOCo(en)(dien)$^{4+}$ [25]4), (dien)$(NH_3)_2$CoOOCo$(NH_3)_2$(dien)$^{4+}$ [26] and (dien)(gly)CoOOCo(gly)(dien)$^{2+}$. The structure of the latter has not been determined, but dien has been shown to prefer a meridional geometry with the secondary amino group occupying a *cis*-peroxo position *(cf. Fig. 5)*. When glycine is replaced by oxalate, yielding the zero-charge complex [(dien)(oxalate)CoOOCo(oxalate)(dien)], the spectrum is drastically altered. The CT band seems to be split into two peaks resulting in spectrum of type *ii*. The bis(oxalato) complex has absorption maxima at 317 and 393 nm both with $\varepsilon \approx 6 \times 10^3$ cm$^{-1}$M$^{-1}$. Such a change has tentatively been explained by assuming the CoOOCo-group to be nonplanar [4]. By torsion of the Co–O bonds around the O–O axis *(Fig. 4)* the distinction between $\pi_h^*$ and $\pi_v^*$ is lost, both become strongly bonding and can give rise to a $\pi^* \rightarrow d_\sigma^*$ LMCT transition of similar intensity.

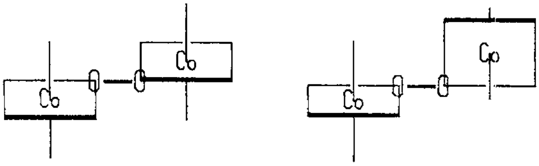

Fig. 4. *Schematic drawing of planar and nonplanar CoOOCo-arrangement in singly bridged μ-peroxo complexes*

Spectra of type *ii* have also been reported of $(his)_2$CoOOCo$(his)_2$ [27] and $(dap)_2$CoOOCo$(dap)_2$ [2] (dap = 2,3-diaminopropionic acid). However, in none of these cases, a structure determination has been carried out.

A few structures have been reported in which the dihedral angle deviates significantly from 180°. In the majority of these cases the Co-centres are coordinated to tetradentate ligands of the *N,N'*-ethylenebis(salicylidenimino)-type [28] [29]. The nonplanarity of the CoOOCo-group may therefore be due to unusual steric constraints rather than to electronic properties of the bridging system. No UV/VIS spectra have

---

4) The crystal structure was determined with a perchlorate. An X-ray diffraction analysis of a dithionate gave identical structural parameters for the cation [26].

been reported. The only nonplanar complex ion with simple ligands is $[(NH_3)_5CoOOCo(NH_3)_5]^{4+}$. While the thiocyanate [30] and the nitrate [31] have a planar arrangement the sulfate [30] deviates from planarity by 40°. *Schaefer* [30] suggested that $(N)_5CoOOCo(N)_5^{4+}$-complexes are normally planar because of electrostatic repulsion of the metal centres. But compensation of the positive charges *via* H-bonding allows the system to revert to its 'natural' torsion. If this theory were correct one should expect the uncharged complexes to be twisted. Yet, for example, $[(dien)(NO_2)_2CoOOCo(NO_2)_2(dien)]$ again has a planar CoOOCo-group just as $[(dien)(NH_3)_2CoOOCo(NH_3)_2(dien)]^{4+}$ (*Fig. 5*), as proved by X-ray diffraction analysis [26]. In doubly bridged µ-peroxo complexes a nonplanar CoOOCo-group is to be expected. In $[(tren)Co(O_2,tren)Co(tren)]^{4+}$ the bridging amine forces the molecule into a bent *transoid*-structure [32]. The deviation from planarity, however, is only 20° and the complex has a spectrum of type *i*. It needs the one-atom bridging ligand $OH^-$ to cause a drastic spectral change: All µ-peroxo-µ-hydroxo complexes investigated so far have spectrum of type *iii* and the dihedral angle of the *cisoid*-CoOOCo-group is close to 60° which principally agrees with the theory of *Lever & Gray* [4].

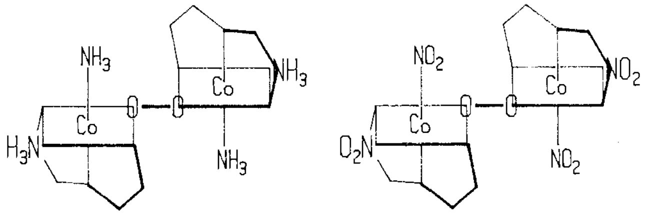

Fig. 5. *Schematic drawings of* $[(dien)(NH_3)_2CoOOCo(NH_3)_2(dien)]^{4+}$ *and* $[(dien)(NO_2)_2CoOOCo(NO_2)_2(dien)]$

While the simple model seems adequate for understanding the principal features of the electronic structure and the UV/VIS absorption of µ-peroxo complexes, it fails to explain the spectra of type *ii* observed frequently in singly bridged species. The singly bridged bis(cyano) complex reported in this communication has a two-band spectrum of type *ii* with absorption maxima at 308 and 398 nm. Apart from a red shift of *ca.* 20 nm the dry crystals exhibit the same characteristic absorption when measured in nujol between silica plates [17]. From these experiments it can be concluded that on dissolution the geometry of the binuclear cation remains essentially unchanged. An explanation for the observed two-band spectrum must therefore be found in the lower symmetry of the ligand field of the two metal centres rather than in a deviation of the CoOOCo-framework from planarity. Type *ii* spectrum is exhibited whenever the coordination spheres containing the amines dien or tren are completed with negatively charged ligands such as oxalate, $HPO_4^{2-}$, $CN^-$ or $NO_2^-$. A similar absorption is observed on oxygenation of $Co(his)_2$ [27] and $Co(dap)_2$ [2] leading to singly bridged µ-peroxo-complexes which must have a dangling carboxylate at each Co-centre [33].

We thank Dr. *V. M. Miskowski*, California Institute of Technology, Pasadena, for helpful discussions. A grant from *Portlandcementfabrik Laufen* enabled him to visit our laboratories. Financial support by the *Swiss National Science Foundation* (project 2.432-0.79) and *Ciba-Geigy AG*, Basel, is also gratefully acknowledged.

## REFERENCES

[1] *A.G. Sykes & J.A. Weil*, Prog. Inorg. Chem. *13*, 1 (1970).
[2] *L.G. Stadtherr, R. Prados & R.B. Martin*, Inorg. Chem. *12*, 1815 (1973).
[3] *G. McLendon & A.E. Martell*, Co-ord. Chem. Rev. *19*, 1 (1976).
[4] *A.B.P. Lever & H.B. Gray*, Acc. Chem. Res. *11*, 348 (1978).
[5] *U. Thewalt & G. Struckmeier*, Z. Anorg. Allg. Chem. *419*, 163 (1976).
[6] *M. Zehnder, U. Thewalt & S. Fallab*, Helv. Chim. Acta *59*, 2290 (1976).
[7] *U. Thewalt, M. Zehnder & S. Fallab*, Helv. Chim. Acta *60*, 867 (1977).
[8] *M. Kabesova, J. Kohout & J. Gazo*, Inorg. Chim. Acta *31*, L435 (1978).
[9] *Z. Dori & R.F. Ziolo*, Chem. Revs. *73*, 247 (1973).
[10] *K.D. Karlin, J.C. Hayes, J.P. Hutchinson & J. Zubiela*, J. Chem. Soc., Chem. Commun. *1983*, 376.
[11] *J. Simplicio & R.G. Wilkins*, J. Am. Chem. Soc. *89*, 6092 (1967).
[12] *M. Mori, J.A. Weil & M. Ishiguro*, J. Am. Chem. Soc. *90*, 615 (1968).
[13] *P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq & M.M. Woolfson*, MULTAN 80 (1980).
[14] *G.M. Sheldrick*, SHELX-76 program, University of Göttingen.
[15] *D.T. Cromer & J.B. Mann*, Acta Crystallogr., Sect. A *24*, 321 (1968).
[16] *D.T. Cromer & D. Liberman*, J. Chem. Phys. *53*, 1891 (1970).
[17] *R. Heiniger*, Thesis, University of Basel, 1983.
[18] *M. Zehnder & S. Fallab*, to be published.
[19] *A.G. Sharp*, 'The Chemistry of Cyano Complexes of the Transition Metals', Academic Press, London, 1976.
[20] *F.R. Fronczek & W.P. Schaefer*, Inorg. Chim. Acta *9*, 143 (1974).
[21] *V.M. Miskowski, J.L. Robbins, I.M. Treitel & H.B. Gray*, Inorg. Chem. *14*, 2318 (1975).
[22] *T. Freedman, G. Yoshida & T.M. Loehr*, J. Chem. Soc., Chem. Commun. *1974*, 1016.
[23] *R.S. Drago & B.B. Corden*, Acc. Chem. Res. *13*, 353 (1980).
[24] *R. Hoffmann, M. Chen & D.L. Thorn*, Inorg. Chem. *16*, 503 (1977).
[25] *J.R. Fritch, G.G. Christoph & W.P. Schaefer*, Inorg. Chem. *12*, 2170 (1973).
[26] *M. Zehnder*, unpublished results.
[27] *S. Bagger & K. Gibson*, Acta Chem. Scand., Ser. A *26*, 3788 (1972).
[28] *M. Calligaris, G. Nardin, L. Randaccio & A. Ripamonti*, J. Chem. Soc. (A) *1970*, 1069.
[29] *A. Lindblom, W.P. Schaefer & R.E. Marsh*, Acta Crystallogr., Sect. B *27*, 1461 (1971).
[30] *W.P. Schaefer*, Inorg. Chem. *7*, 725 (1968).
[31] *U. Thewalt*, Z. Anorg. Allg. Chem. *485*, 122 (1982).
[32] *M. Zehnder, U. Thewalt & S. Fallab*, Helv. Chim. Acta *62*, 2099 (1979).
[33] *R.G. Wilkins*, Adv. Chem. Ser. *100*, 111 (1971).