that, unlike the parent complex, which exhibits a conductivity value expected for a 2:1 electrolyte (Λ_M = 240 Ω^{-1} cm^{-1} mol^{-1} for 8 × 10^{-4} M complex in acetonitrile), the peroxide complex behaves like a 1:1 electrolyte (Λ_M = 147 Ω^{-1} cm^{-1} mol^{-1} for 8 × 10^{-4} M complex in acetonitrile).[64] We thus propose that peroxide binding appears to result in the replacement of the μ-OH with a μ-η^1:η^1 peroxide moiety with the retention of the basic ligand coordination around the dibridged dinuclear center (Figure 7a). This proposed structure for $[Fe_2(HPTB)(O_2)(NO_3)_2]NO_3$ is different from that proposed for the dioxygen adduct of $[Fe_2(N\text{-Et-HPTB})(OBz)](BPh_4)_2$,[27] which consists of a tribridged diferric core analogous to the 2+ cation in Figure 7b with benzoate replacing nitrate. The structural differences in the two peroxide complexes may be reflected in the subtle changes in their UV–vis, Raman, and Mössbauer parameters (Tables III and IV).

All of the diferric peroxide complexes studied thus far appear to favor peroxide bridge formation, and none of these complexes model the dioxygen-binding mode found for oxyhemerythrin.[8,26-28,56] Those capable of reversible dioxygen binding derive from monoferrous precursor complexes and presumably have trans μ-η^1:η^1-peroxo coordination.[25,26] The diferric peroxide complexes derived from dinucleating ligands such as HPTB and HXTA are most likely to have cis μ-η^1:η^1 peroxide coordination and appear incapable of reversible dioxygen binding. They are reactive toward organic substrates[29,30] and may thus more appropriately model the diiron–dioxygen interactions in ribonucleotide reductase and methane monooxygenase, diiron proteins that activate dioxygen.[4,10] A detailed study of the reactivity of the $[Fe_2(HPTB)(OH)(NO_3)_2](NO_3)_2$/peroxide complex toward organic substrates is in progress.

Acknowledgment. This work was supported by the National Institutes of Health through Grants GM-38767 (L.Q.) and GM-22701 (Eckard Münck), a predoctoral traineeship for B.A.B. (Grant GM-08277), and a postdoctoral fellowship for A.E.T. (Grant GM-12792), and by the E. G. Schleider Educational Foundation (C.J.O.). Beamline X9A at NSLS is supported by the National Biostructures PRT under NIH Grant RR-01633. We are grateful for Professor James Terner's assistance in preparing the isotopically labeled hydrogen peroxide and for Dr. Robert Kean's assistance in assembling the low-temperature resonance Raman equipment.

---

(63) Brennan, B. A.; Chen, Q.; Que, L., Jr. Unpublished results.
(64) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81-122.

Contribution from the Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria,
Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria,
and Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciencies, 1040 Sofia, Bulgaria

Chelating Modes of 3-Substituted 2,4-Pentanediones. Crystal and Electronic Structure of Bis(3-cyano-2,4-pentanedionato)cobalt(II)

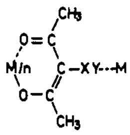
Olyana Angelova,*,† Josef Macicek,‡ Michail Atanasov,§ and Galin Petrov†

Received May 25, 1990

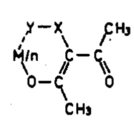
Coordination modes of 3-substituted 2,4-pentanediones are considered with respect to the chemical nature of the substituent and the conformational flexibility of the ligand. Examples of additional and competitive coordination of the extra donor site(s) are given, and two different pathways for the structural rearrangement in such complexes are discussed. Accordingly, a new constitution of the acetylacetone cyanation intermediate product **4** in its Cu and Ni complexes is speculated. The 3D network structure of the title compound in which all functional groups are involved in coordination is determined ($C_{12}H_{12}CoN_2O_4$, tetragonal, space group $P4_2/n$, a = 14.444 (1) Å, c = 6.832 (2) Å, D_x = 1.431 g cm^{-3}, Z = 4, R = 0.0217), and its solid-state electronic spectrum is analyzed in terms of the angular overlap model.

Introduction

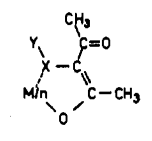
The structure and stability of 3-substituted 2,4-pentanedionato chelate complexes are influenced by the electron-withdrawing strength of the substituent to different extents.[1] For instance, nitro, cyano, and halogeno groups cause an electron density shift away from the central atom[2] and weakening of the coordinate bonds.[3] As a result, the prerequisites for the formation of additional (with preservation of the O,O-chelate; **1**) or competitive (toward a carbonyl group; **2**, **3**) coordination of the substituent are established.



1



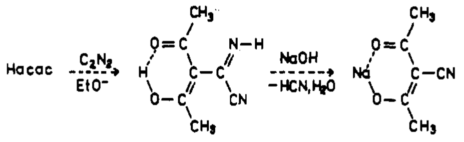
2



3

Type **1** intermolecular bonding is realized in the $[(NH_3)_5CoNCacacCr]^{4+}$ complex cation,[4] where NCacacH = 3-cyano-2,4-pentanedione (XY = CN). Recently, we reported the structure of $Cu(NCacac)_2$,[5,6] in which one of the cyano groups is linked to an adjacent copper atom. The presence of intramolecular additional coordination of the hexafluorobut-2-enyl substituent (XY = $CF_3C{=\!=}CCF_3$) to iridium and rhodium atoms has been reported by Russell et al.[7]

Scheme I



4 5

---

† University of Sofia.
‡ Institute of Applied Mineralogy, BAS.
§ Institute of General and Inorganic Chemistry, BAS.

(1) (a) Tsiamis, C.; Cambanis, S.; Hadjikostas, C. *Inorg. Chem.* **1987**, *26*, 26. (b) Tsiamis, C.; Cambanis, S.; Jannakoudakis, A. D.; Theodoridou, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *252*, 109.
(2) Sahai, R.; Verma, R. *J. Indian Chem. Soc.* **1981**, *58*, 640.
(3) Tanaka, M.; Shono, T.; Shinra, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3190.
(4) Balahura, R. J.; Johnston, A. J. *Inorg. Chem.* **1983**, *22*, 3309.
(5) Angelova, O.; Petrov, G.; Macicek, J. *Acta Crystallogr.* **1989**, *C45*, 710.
(6) Such bridging behavior of the cyanoacetylacetonato ligand was earlier reported by Thompson et al. from spectroscopic analysis of zirconium and titanium complexes: (a) Thompson, D. W.; Barrett, P. B.; Lefelhocz, J. P.; Lock, G. A. *J. Coord. Chem.* **1973**, *3*, 119. (b) Lock, G. A.; Thompson, D. W. *J. Chem. Soc., Dalton Trans.* **1980**, 1265.
(7) (a) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1749. (b) Barlex, D. M.; Evans, J. A.; Kemmitt, R. D. W.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1971**, 331.

0020-1669/91/1330-1943$02.50/0

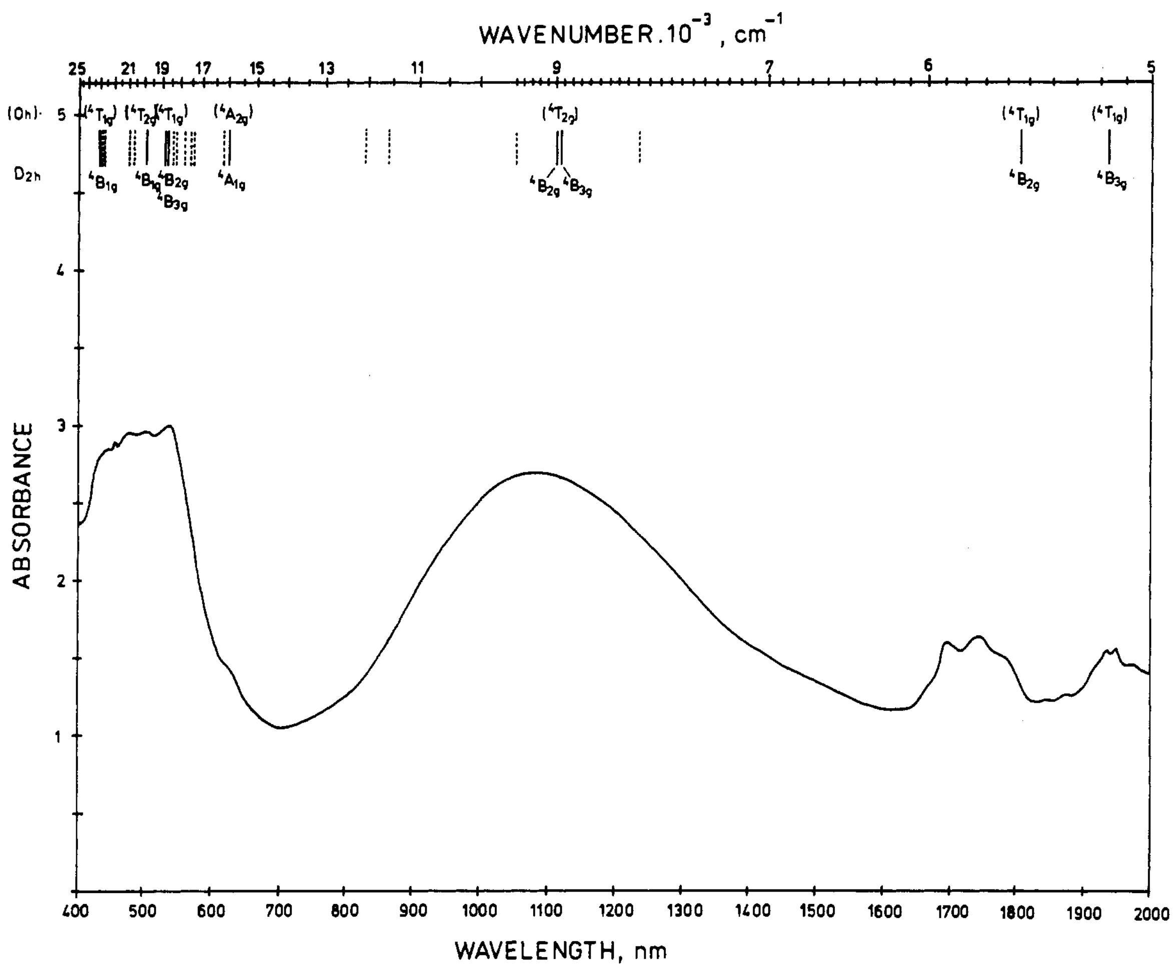


Figure 1. Solid-state electronic spectrum of $Co(NCacac)_2$ at 298 K. Calculated d–d transition energies originating from quartet and doublet levels are marked by solid and dotted lines, respectively. Assignment of the spin-allowed transitions in the D_{2h} point group and their parent O_h term symmetry is also indicated. Best fit parameters: $e_\sigma{}^{N} = 3100\ (200)\ cm^{-1}$; $e_\sigma{}^{O} = 2400\ (100)\ cm^{-1}$; $e_{\pi\parallel}{}^{O} = 805\ (35)\ cm^{-1}$; $e_{\pi\perp}{}^{(N,O)} = -680\ (35)\ cm^{-1}$; $B = 645\ (43)\ cm^{-1}$; $\zeta = 0$. Numbers in parentheses are the errors in the least significant digits.

Complexes with competitive bonding (type **2** or **3** chelate rings) whose structure was confirmed by X-ray analysis are also known. In two palladium complexes, $Pd(XYacac)_2$ and Pd(XYacac)(DMAMP)[8] (XY = $CF_3C{=}CCF_3$ as above), the O,O-chelate rings have been found to undergo transformation to the six-membered O,C-chelates **2**. The release of one of the carbonyl groups from coordination is more favored by such 3-substituents, which contain more than one coordinating site and thus make the ligand potentially compartmental.[9,10] Five-membered chelate rings occur in 3-(hydroxyimino)-2,4-pentanedionato complexes $M(XYacac)_2B_2$ (M = Fe,[11] Co;[12] B = N-base). The oxyimino group (XY = NO) coordinates through the N atom, as is common for the oximato complexes.[13]

The coordination modes of different 3-substituted acetylacetones considered above will be employed to revise the coordination behavior of 3-(cyanoiminomethyl)-2,4-pentanedione (**4**; XY = C(CN)NH), an intermediate product in the cyanation reaction of acetylacetone[14] (Scheme I). Pathways for possible structural rearrangements of **4** and an alternative interpretation of the structures of its Cu and Ni complexes, earlier reported by Corain et al.,[15] will be given. The occurrence of intermolecular bonding of type **1** will be illustrated for the title complex $Co(NCacac)_2$.

Experimental Section

Reagents. Freshly distilled 2,4-pentanedione, anhydrous $CoCl_2$, NaOH, and HCl (Merck, p.a.) were used as reactants. Ethanol dried over Mg turnings and freshly distilled was used as the solvent. Cyanogen was obtained by dropwise addition of concentrated KCN solution to $CuSO_4{\cdot}5H_2O$.

Instruments. Infrared spectra were recorded as Nujol mulls on a Specord M80 spectrometer. Electronic absorption spectra were measured on a Perkin-Elmer Model 330 spectrophotometer. Magnetic susceptibility was measured in the 140–470 °C range on a locally designed magnetic balance by using the Faraday technique. Elemental analyses were performed by the Microanalytical Laboratory of the Chemistry Department of the University of Sofia.

Preparation of Sodium 3-Cyano-2,4-pentanedionate, NCacacNa (5). The acacH cyanation procedure of Fackler[14] was carefully followed (Scheme I). The imido product **4** was treated with sodium hydroxide, and the mixture was neutralized with hydrochloric acid. After the solvent was removed under reduced pressure, however, the diketonate sodium salt was obtained instead of the expected NCacacH. It was recrystallized

---

(8) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1743.

(9) Svensson, Ch.; Ymen, I. *Cryst. Struct. Commun.* **1981**, *10*, 423.

(10) Matsumoto, N.; Tsutsumi, T.; Ohyoshi, A.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1388.

(11) Figgis, B. N.; Raston, C. L.; Sharma, R. P.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 2431.

(12) Tamura, H.; Ogawa, K.; Ryu, R.; Tanaka, M.; Shono, T.; Masuda, I. *Inorg. Chim. Acta* **1981**, *50*, 101.

(13) Bose, K. S.; Sharma, B. C.; Patel, C. C. *Inorg. Chem.* **1973**, *12*, 120.

(14) (a) Fackler, J. P. *J. Chem. Soc.* **1962**, 1957. (b) The procedure was originally proposed by: Traube, W. *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 2938.

(15) (a) Corain, B.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1979**, *18*, 3523. (b) Corain, B.; Crotti, C.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1981**, *20*, 2044. (c) Corain, B.; Basato, M.; Visentin, G.; Zanotti, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1217. (d) Corain, B.; Basato, M.; Marcomini, A.; Klein, H. F. *Inorg. Chim. Acta* **1983**, *74*, 1. (e) Corain, B.; Basato, M.; Del Zotto, A.; Zanotti, G. *Inorg. Chem.* **1983**, *22*, 2749. (f) Corain, B.; Basato, M.; Ballota, C.; Ahmed, M. *Inorg. Chim. Acta* **1984**, *87*, 105. (g) Corain, B.; Basato, M.; Mori, E.; Valle, G. *Inorg. Chim. Acta* **1983**, *76*, L277. (h) Basato, M.; Corain, B.; Marcomini, A.; Valle, G.; Zanotti, G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 965. (i) Basato, M.; Corain, B.; Veronese, A. C.; Angeli, F. D.; Valle, G.; Zanotti, G. *J. Org. Chem.* **1984**, *49*, 4696.

from ethanol and identified on the basis of its IR spectrum (selected stretching vibrations, cm^{-1}): C—C, 1274 (w); C—CN, 1350 (s); C—O, 1538 (vs); C—C, 1643, 1659 (vs); C≡N, 2220 (vs). An average shift of 6 cm^{-1} was observed for all bands in the spectrum, in comparison to the data of Wierzshowski and Shugar.[16] The compound is stable up to 250 °C, in contrast to NCacacH, melting at 54 °C.[14b] Anal. Calc for $C_6H_6NNaO_2$: C, 48.99; H, 4.11; N, 9.52. Found: C, 47.86; H, 4.14; N, 8.97.

Preparation of Bis(3-cyano-2,4-pentanedionato)cobalt(II), Co(NCacac)$_2$. Solid anhydrous $CoCl_2$ (0.390 g, 3 mmol) was added to a solution of NCacacNa (0.880 g, 6 mmol) in dry ethanol (50 mL). The originally blue solution turned violet and then pink-red. The reaction mixture was left overnight in the dark. Red-orange crystals, suitable for X-ray analysis, appeared in the reddish pink solution. The crystals are insoluble in common organic solvents and very slightly soluble in ethanol and methanol. IR stretching frequencies (KBr, cm^{-1}): C═C, 1285 (w); C—CN, 1353 (vs); C—O, 1527 (d, vs); C—C, 1610, 1620, 1630 (vs); C≡N, 2240 (vs). The magnetic moment of Co(NCacac)$_2$ is $\mu_{eff} = 3.957$ μ_B, much lower than the values for the corresponding Co(acac)$_2$·nH$_2$O compounds.[17] In the measured temperature range the Co(NCacac)$_2$ complex obeys the Curie–Weiss law, $\chi_M = C/(T - \Theta)$, $\Theta = 16.41$ K. The absorption spectrum of the solid compound is shown in Figure 1. Anal. Calc for $C_{12}H_{12}CoN_2O_4$: C, 46.92; H, 3.94; N, 9.12. Found: C, 46.82; H, 3.84; N, 9.02.

The reaction between solid anhydrous $NiCl_2$ and NCacacNa under similar conditions produced two types of crystals. The X-ray powder diagram of the first type indicated that they were isostructural with Co(NCacac)$_2$,[18] and the analytical data of the others were consistent with the formula Na[Ni(NCacac)$_3$]·EtOH. Anal. Calc for Na[$C_{18}H_{18}NNiO_6$]·C_2H_6O: C, 48.03; H, 4.84; N, 8.40. Found: C, 47.12; H, 4.46; N, 8.27.

Ligand-Field Analysis. The solid-state electronic spectrum of Co(NCacac)$_2$ is explained in terms of an extended angular overlap model[19-21] (AOM), which considers π interactions between metal d and ligand π orbitals and the detailed angular geometry simultaneously.[21,22] Energy levels were calculated by an AOM program within the 120-fold basis of the d^7 configuration. The ligand-field matrix parametrized the influences from axial (N) and equatorial (O,O) ligands by using two distinct sets of parameters for σ (e_σ) and π ($e_{\pi\perp}$ and $e_{\pi\|}$) interactions for each ligand. Parallel and perpendicular were defined with respect to the chelate plane and referred to the in-plane d_{xy} ($e_{\pi\|}$) and out-of-plane d_{xz}, d_{yz} ($e_{\pi\perp}$) orbitals, respectively. All configuration interactions due to interelectron repulsion (Racah B and C parameters), spin–orbit coupling (ζ), and the low-symmetry ligand field were accounted for. Assignment of quartet-state energies (Mulliken notation for the D_{2h} point group, $\zeta = 0$) was made by using explicit formulas for the quartet matrices. The geometry of the CoO_4N_2 moiety was established by two structural angles: the chelate bite angle α = OMO = 86.6° and the dihedral angle ψ = 52.6° between the axial chelate plane and the xz plane.

A further distinction among the out-of-plane π interactions was made in terms of the phase-coupling model,[22,23] introducing equal or opposite signs for the atomic orbital coefficients of the relevant molecular orbitals of the chelate. Two out-of-plane π-bonding parameters, $e_{\pi\perp}$ for in-phase and $e_{\pi\perp}'$ for out-of-phase coupling molecular orbitals, were used. In the case of acacH, these parameters are related to the HOMO ($e_{\pi\perp}{}^{O}$) and LUMO ($e_{\pi\perp}{}^{O'}$) frontier orbitals, respectively.[20]

Ligand-field term energies including doublet states with $C/B = 4.63$ (free ion ratio[24]) for a wide range of parameter values were calculated within the AOM model in order to achieve agreement with the experimental ligand-field transitions. The use of different parameters $e_{\pi\perp}{}^{N}$ and $e_{\pi\|}{}^{N}$ describing the π anisotropy for N was precluded by the assumption of sp hybridization of the N atom. The insensitivity of the term energies to this π anisotropy is easily explainable on the basis of the small deviation of the ψ angle from 45°, implying pseudoisotropic π behavior.

Table I. Crystal Data for Co(NCacac)$_2$

$C_{12}H_{12}CoN_2O_4$	D_x = 1.431 g·cm^{-3}
fw = 307.17	λ(Mo Kα) = 0.71073 Å
tetragonal	μ = 12.09 cm^{-1}
space group $P4_2/n$ (No. 86)	$F(000)$ = 628
a = 14.444 (1) Å[a]	T = 292 K
c = 6.832 (2) Å[a]	R = 0.0217
V = 1423.9 (7) Å^3	R_w = 0.0227
Z = 4	

[a] Symmetry-constrained unit cell parameters as calculated with the program BLAF[26] are given. They differ only slightly from the X-ray powder values obtained from the refinement of 2θ positions of 47 reflections:[18] a = 14.453 (2), c = 6.837 (3) Å.

Table II. Positional and Equivalent Isotropic Thermal Parameters for Co(NCacac)$_2$[a]

atom	x	y	z	B_{eq}, Å^2
Co	0.000	0.000	0.000	1.899 (7)
O(1)	0.0338 (1)	0.1278 (1)	0.1077 (3)	2.57 (3)
O(2)	−0.0710 (1)	0.0686 (1)	−0.2143 (3)	2.78 (4)
N(7)	0.0077 (2)	0.3761 (1)	−0.3313 (4)	3.27 (5)
C(1)	0.0389 (2)	0.2014 (2)	0.0137 (4)	2.38 (4)
C(2)	−0.0594 (2)	0.1501 (2)	−0.2722 (4)	2.48 (5)
C(3)	−0.0036 (2)	0.2159 (2)	−0.1726 (4)	2.24 (5)
C(4)	0.0042 (2)	0.3052 (2)	−0.2590 (4)	2.60 (5)
C(5)	0.0918 (2)	0.2794 (2)	0.1074 (5)	3.94 (6)
C(6)	−0.1087 (3)	0.1777 (2)	−0.4581 (5)	5.03 (7)

[a] Numbers in parentheses are errors in the least significant digits.

Further reduction of the number of adjustable parameters was made by using the following arguments:

(i) Since the out-of-plane π orbitals of the coordinating oxygen and nitrogen atoms form a common conjugated π system, we assumed that

$$e_{\pi\perp}{}^{O} = e_{\pi\perp}{}^{N} = e_{\pi\perp}{}^{(O,N)}$$

(ii) The D_{2h} symmetry of the CoO_4N_2 chromophore is best seen in the additional splitting of 750 cm^{-1} in the 5000–6000-cm^{-1} region. The calculations showed that the deviation of α from 90° was large enough to give an energy difference between the corresponding levels of 400 cm^{-1} and the remaining 350 cm^{-1} had to be explained by orbital phase coupling. This gave us an additional relation between the AOM parameters:[25]

$$e_{\pi\perp}{}^{O} = e_{\pi\perp}{}^{O'}$$

With the remaining parameters, it was found that the quartet $^4T_1$ (ground state) and $^4T_2$ splittings are most sensitive to the e_π parameters whereas B affects mainly the $^4T_1$ excited-state energy. Using B, $e_\sigma{}^{N}$, $e_\sigma{}^{O}$, $e_{\pi\|}{}^{O}$, and $e_{\pi\perp}{}^{(N,O)}$ as variables led to a unique fit to the eight experimental d–d transition energies. Calculated and experimental energy levels are compared in Figure 1.

Structure Solution and Refinement. A red-orange prismatically shaped crystal with approximate dimensions 0.08 × 0.08 × 0.11 mm was glued onto a glass capillary and analyzed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation at 292 K. Cell constants were obtained from a least-squares refinement of the setting angles of 22 reflections in the range $18.0 < \theta < 20.0°$. Crystal data are given in Table I. The intensities of three standard reflections were monitored every 2.0 h during X-ray exposure, and the crystal orientation was checked systematically. A total of 3037 reflections (excluding standards) were collected in the range $(\sin \theta)/\lambda < 0.616$ Å^{-1} (h = 0–17, k = 0–17, l = 8̄–8). Intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu r < 0.14$). Intensity of the standard reflections varied within 1%, and therefore no decay correction was applied. The symmetrically equivalent reflections were merged; $R_{int}(F)$ = 0.018. From 1530 unique reflections, 886 reflections with $I > 3\sigma(I)$ were considered observed and used in further calculations.

---

(16) Wierzshowski, K. L.; Shugar, D. *Spectrochim. Cosmochim. Acta* **1965**, *21*, 943. The $\nu_{C\equiv N}$ band at 2220 cm^{-1} is, in fact, shifted by 42 cm^{-1} from the reference value.

(17) Cotton, F. A.; Holm, R. H. *J. Am. Chem. Soc.* **1960**, *82*, 2979.

(18) Macicek, J. JCPDS Grant-in-Aid Report, Bulgarian Academy of Sciences, Sofia, Bulgaria, 1989; PDF Card No. 40-1821.

(19) Ceulemans, A.; Dendooven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1153.

(20) Atanasov, M.; Schonherr, T.; Schmidtke, H.-H. *Theor. Chim. Acta* **1987**, *71*, 59.

(21) Atanasov, M. A.; Schonherr, T. *Inorg. Chem.* **1990**, *29*, 4545.

(22) Lee, K.-W.; Hoggard, P. E. *Chem. Phys.* **1989**, *135*, 219.

(23) Moucharafieh, N. C.; Eller, P. G.; Bertrand, J. A.; Royer, D. J. *Inorg. Chem.* **1978**, *17*, 1220.

(24) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition Metal Ions in Crystals*; Academic Press: New York, 1970.

(25) These assumptions are consistent with simple Huckel calculations on acacH and NCacacH. The MO diagrams of both ligands in their enol form show that the π-electronic structure of NCacacH is largely modified by the out-of-plane π-acceptor behavior of the CN substituent, as compared to the case of nonsubstituted acacH. The two LUMO levels in NCacacH with different phase properties become very close in energy, implying a phase decoupling and restoration of the additivity of the ligand field.

(26) Yordanov, A.; Macicek, J. Collected Abstracts of the 12th ECM, Moscow, Aug 20–29, 1989; Vol. 3, p 196.

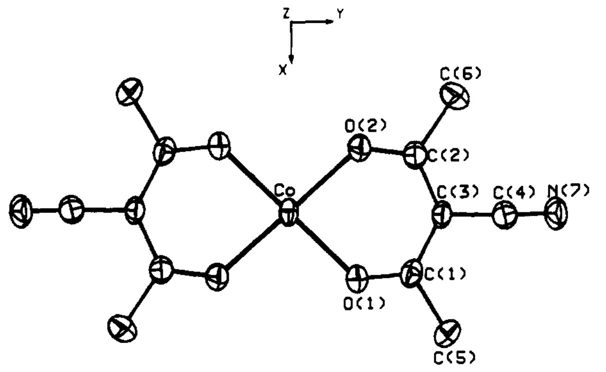


Figure 2. Atom-numbering scheme and choice of the coordination axes for the AOM calculations. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted.

Table III. Interatomic Distances (Å) and Angles (deg)[a]

Co–O(1)	2.046 (2)	N(7)–C(4)	1.138 (3)
Co–O(2)	2.044 (2)	C(1)–C(3)	1.430 (5)
Co–N(7)	2.132 (2)	C(1)–C(5)	1.503 (4)
O(1)–C(1)	1.245 (3)	C(2)–C(3)	1.420 (4)
O(2)–C(2)	1.253 (3)	C(2)–C(6)	1.511 (5)
		C(3)–C(4)	1.424 (4)
O(1)–Co–O(1)	180.1 (4)	O(1)–C(1)–C(3)	124.0 (3)
O(1)–Co–O(2)	86.56 (7)	O(1)–C(1)–C(5)	116.8 (3)
O(1)–Co–N(7)	93.04 (9)	C(3)–C(1)–C(5)	119.3 (3)
O(2)–Co–O(2)	180.1 (3)	O(2)–C(2)–C(3)	123.7 (3)
O(2)–Co–N(7)	89.49 (9)	O(2)–C(2)–C(6)	116.8 (3)
N(7)–Co–N(7)	180.1 (4)	C(3)–C(2)–C(6)	119.6 (3)
Co–O(1)–C(1)	126.8 (2)	C(1)–C(3)–C(2)	125.0 (2)
Co–O(2)–C(2)	127.9 (2)	C(1)–C(3)–C(4)	117.9 (3)
Co–N(7)–C(4)	171.1 (3)	C(2)–C(3)–C(4)	117.0 (3)
		N(7)–C(4)–C(3)	177.7 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The structure was solved by MULTAN82, which revealed the positions of all non-hydrogen atoms. The initial model was refined routinely by full-matrix least squares by minimizing the $\sum w(|F_o| - |F_c|)^2$ function with unit weights. Hydrogen atoms were refined isotropically. Convergence was reached at $R = 0.0217$ and $R_w = 0.0227$, and the correctness of the space group choice was thus confirmed. The goodness of fit was $S = 0.805$, and the maximum least-squares shift-to-error ratio in the final refinement cycle was 0.07. The highest positive and negative peaks in the final difference Fourier map were 0.155 and -0.237 e·Å^{-3}. No correction for secondary extinction was applied. Neutral-atom scattering factors and anomalous-dispersion corrections were applied as coded in the SDP/PDP V3.0 crystallographic package.[27] All calculations were carried out on a PDP-11/44 computer at the Institute of Applied Mineralogy. The final atomic coordinates are given in Table II. The atom-numbering scheme is presented in Figure 2. Selected interatomic distances and angles are summarized in Table III.

Results

Description of the Structure. The structure represents a 3D net of centrosymmetric Co(NCacac)$_2$ molecules in which the ligand performs both chelating and intermolecular linking functions (Figure 3). The molecules are arranged along the 4_2 axes in a double-helical fashion with a screw period of 2 times the c parameter. Every molecule belongs to two adjacent helices which in the centric space group possess an opposite chirality. The cobalt atoms are disposed at the points of an I-centered sublattice with a half-volume of the unit cell. The shortest Co···Co distances are 6.832 (2) Å (c parameter length) and 7.989 (2) Å (half of the ac and bc face diagonals).

The cobalt atom has a tetragonally elongated octahedral coordination of four oxygen atoms in the equatorial plane and two nitrogen atoms at the apices. Co–O distances of 2.046 (2) and 2.044 (2) Å correspond well with the average Co–O bond lengths found in cobalt(II) acetylacetonates.[28] The intermolecular Co–N distance of 2.138 (3) Å is shorter than the respective bond lengths in the mixed Co(acac)$_2$(N-base)$_2$ complexes with similar coordination geometry (2.154–2.262 Å range).[29] Formation of such a short Co–N distance is reflected in the value of $\nu_{C\equiv N} = 2240$ cm^{-1} as compared to 2220 cm^{-1} for noncoordinated NCacacH.[14,16]

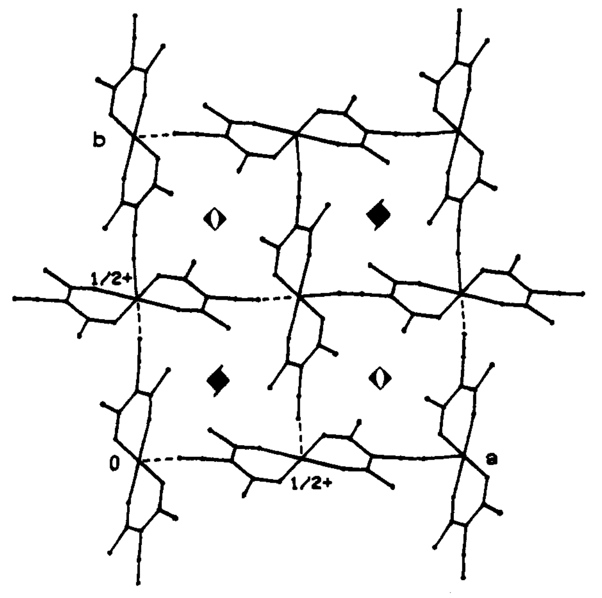


Figure 3. Projection of the structure onto the ab plane. Bonds to molecules translated along the c axis are shown by dashed lines. The symbols of the $\bar{4}$ and 4_2 axes are added for the sake of clarity.

The geometry of the ligand resembles that of analogous acetylacetonato complexes.[28,29] The chelate ring adopts a half-chair conformation with Co displaced 0.47 Å from the ligand (planar within 0.03 Å). In the Co(acac)$_2$·nH$_2$O series, this cobalt atom shift is also within 0.14–0.47 Å. The folding angle along the O···O line is 161.04 (3)°. The bond lengths and angles are interpretable in terms of a significant π-electron delocalization and fit the data for various metal acetylacetonates.[28,30] The low accuracy of the published structural data on cobalt acetylacetonates, however, makes it difficult to trace the influence of the cyano group on the ring geometry. The closeness of the average C–O bond lengths in the present compound (1.249 (3) Å) and in [(NH$_3$)$_5$CoNCacac](Cl)(ClO$_4$)·2H$_2$O (1.248 (7) Å),[31] where neither of the carbonyl groups coordinates to the metal, is noteworthy. In Co(acac)$_2$·nH$_2$O complexes,[28a] the corresponding average value is 1.267 (3) Å. The length of the C(3)–C(4) bond (1.424 (4) Å) is close to that for the bridging ligand (1.428 (4) Å) but differs from that in the noncoordinated ligand (1.443 (4) Å) in the Cu(NCacac)$_2$ complex.[5] Both values are, however, significantly longer than the corresponding one in [(NH$_3$)$_5$CoNCacac](Cl)(ClO$_4$)·2H$_2$O (1.405 (8) Å). The ligand plane is tilted toward the bc, ac, and ab faces of the unit cell by 34.59 (5), 89.37 (4), and 55.28 (5)°, while the CoO$_4$ plane is at 33.83 (4), 107.62 (3), and 62.06 (5)°, respectively.

The C(4)–N(7)···Co angle of 171.1 (3)° deviates insignificantly from linearity, as expected for the N(sp)···Co(d_{z^2}) interaction. This

---

(27) *SDP User's Guide*; B. A. Frenz & Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland, 1985.

(28) (a) Selected average bond lengths and angles within the ring of the four Co(acac)$_2$·nH$_2$O (n = 0–2) compounds known so far: Co–O = 2.052, O–C = 1.267, C–C$_i$ = 1.422, C–C$_x$ = 1.529 Å; O–Co–O = 90.0, O–C–C$_i$ = 125.2, O–C–C$_x$ = 116.3, C–C$_i$–C = 125.1°. (b) Cottom, F. A.; Elder, R. C. *Inorg. Chem.* **1965**, *4*, 1145. (c) Cotton, F. A.; Eiss, R. *J. Am. Chem. Soc.* **1968**, *90*, 38. (d) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1966**, *5*, 423. (e) Bullen, G. J. *Acta Crystallogr.* **1959**, *12*, 703.

(29) (a) Bertrand, J. A.; Kalyanaraman, A. R. *Inorg. Chim. Acta* **1971**, *5*, 167. (b) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 1117. (c) Hursthouse, M. B.; Malik, K. M.; Davies, J. E.; Harding, J. H. *Acta Crystallogr.* **1978**, *B34*, 1355. (d) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Rathby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307.

(30) Lingafelter, E. C.; Braun, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 2951.

(31) Balahura, R. J.; Ferguson, G.; Johnston, A.; Ruhl, B. L. *Polyhedron* **1986**, *5*, 2075.

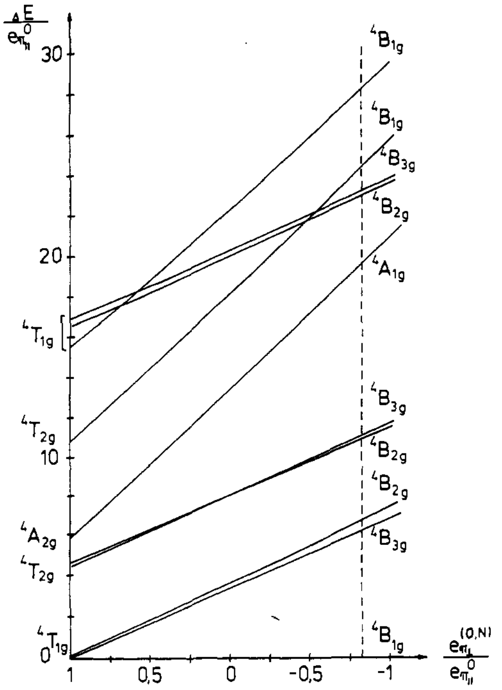


Figure 4. Term energies for the *trans*-CoO_4N_2 chromophore in D_{2h} symmetry versus $e_{\pi\perp}{}^{(O,N)}$ (both in units of $e_{\pi\parallel}{}^{O}$) with constant values for the remaining parameters. Correspondence with the experimental transition energies from Figure 1 is shown by a dashed line.

linkage in the layered $Cu(NCpaac)_2$[32] (NCpaacH = di-*O*-propyl ester of (1-cyano-2-oxopropyl)phosphonic acid) and chainlike $Cu(NCacac)_2$ complexes[5] adopts a less suitable geometry (149.8 (9) and 115.7 (2)°, respectively). The C(4)–N(7) distance of 1.138 (3) Å falls within the range 1.113 (12)–1.146 (4) Å ascertained for coordinated cyano groups in many different compounds[15a,c33] but is shorter than the free-group value of 1.155 Å.[34] The observed bond shortening is in accordance with the C≡N bond strength increase upon coordination.[35]

Electronic Spectra. $Co(NCacac)_2$ is an appropriate model for testing π-bonding concepts[20,23,36,37] because the parent octahedral $^4T_{1g}$ ground state is of π type and may undergo ligand-field splittings large enough to be detected spectroscopically. Ligand-field spectra of d^7 chromophores like CoL_6 (L = H_2O, NH_3, en/2) with high-spin configurations show bands in the ranges 8100–11 000, 16 000–18 000, and 19 400–22 000 cm^{-1} originating from the transitions $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), $^4A_{2g}$ (F), and $^4T_{1g}$ (P), respectively.[38,39] The corresponding electronic transitions in anhydrous $Co(acac)_2$[17] and $Co(acac)_2(H_2O)_2$[40] also fall in the regions mentioned. The solid reflectance spectrum of $Co(NCacac)_2$ in the visible and near-IR regions (Figure 1) is consistent with these observations but shows band maxima in the long-wave part around 5000–6000 cm^{-1} which cannot be understood in terms of the usual octahedral scheme. Since differences due to σ-bonding interactions of the O and N ligands are less important for the splitting of the d levels with T_1 or T_2 parent O_h symmetry,[21] the transitions at 5000–6000 cm^{-1} have to be regarded as due to $^4T_{1g}$ ground-state and/or $^4T_2$ excited-state splitting π effects.

The variations of the $e_{\pi\parallel}{}^{O}$ and $e_{\pi\perp}{}^{(N,O)}$ parameters are most important for the observed T_{1g} and T_{2g} splittings, which can lead back to the energy difference between the d_{xy} and d_{xz},d_{yz} orbital energies:

$$E(d_{xy}) - E(d_{xz},d_{yz}) = 4e_{\pi\parallel}{}^{O} - 4e_{\pi\perp}{}^{(N,O)}$$

Since $e_{\pi\parallel}{}^{O}$ is greater than zero,[41] implying π-donor behavior for the in-plane oxygen lone pair, it follows that our results are only consistent with π-acceptor out-of-plane π interactions Co–N,O. The dependence of the quartet-state energies on the $e_{\pi\perp}{}^{(O,N)}/e_{\pi\parallel}{}^{O}$ ratio, depicted in Figure 4, is in accordance with this conclusion and serves as a basis for the interpretation of the spectrum in Figure 1. Figures showing the term energy dependence on the remainder of the parameters are not worth presenting, since the term splittings are practically independent of their variation. The bands at 5250 and 5850 cm^{-1} are due to the transitions $^4B_{1g} \rightarrow {}^4B_{3g}$ and $^4B_{2g}$, respectively, within the ground-state T_{1g} manifold. The energy difference between these two transitions reflects the small yet nonnegligible influence of the angle α, deviating from 90°. A further splitting of the quartet levels to $\pm^3/_2$ and $\pm^1/_2$ sublevels results from spin–orbit coupling and may explain the doublet structure of both bands in this region.

The spin–orbit coupling constant of –470 cm^{-1}, resulting from this structure, compares well to the free-ion value –533 cm^{-1},[24] being slightly reduced as in other low-symmetry Co(II) complexes.[37] The broad band at 9300 cm^{-1} is assigned to the transitions $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{3g}$ from the parent T_{2g} octahedral term, and the shoulder at 16 000 cm^{-1} is assigned to the $^4B_{1g} \rightarrow {}^4A_{1g}$ transition, corresponding to a two-electron jump from the t_{2g} to the e_g level. There are at least four transitions seen in the spectrum between 18 000 and 23 000 cm^{-1} which are interpreted as split components of the $^4T_{1g}$ (F) → $^4T_{1g}$ (P) transition in O_h geometry and one component ($^4B_{1g} \rightarrow {}^4B_{1g}$) from the T_{2g} term.

The AOM parameters (Figure 1) compare well with literature data on Co–L bonding parameters (L = N, O) for hexacoordinate Co(II) chromophores extracted on the basis of ESR measurements and their AOM interpretations.[42] σ-Bonding parameters for Co–O are also consistent with those reported for a five-coordinate Co(II) ion,[37] being lowered by the longer Co–O distances. They also give realistic Δ = 10*Dq* values according to the expression

$$10Dq = 3e_\sigma - 2e_{\pi\perp} - 2e_{\pi\parallel}$$

namely, 11 880 and 6800 cm^{-1} for 10*Dq*(N) and 10*Dq*(O), respectively, the first of which can be compared to the value for CH_3CN (10 550 cm^{-1} [39]). The value of the Racah *B* parameter, 645 cm^{-1}, is suggestive of a large nephelauxetic reduction (971 cm^{-1} for the free Co(II) ion[24]), in contrast to the values for a series of cobaltous β-diketonates[40] with slightly reduced *B* parameters. Similar lowering of the *B* value has been observed in some chromium(III) chelate complexes.[43]

Discussion

The results of spectroscopic and structural investigations of various chelate complexes containing the NCacac ligand reveal the existence of monomeric, oligomeric,[6] chainlike and 3D-network species. In all of them, the NCacac ligand performs its O,O-chelating function but the participation of the cyano group in coordination makes the complexes different. Monomeric complex units are formed when the coordination environment of the metal ion is completed by other ligands without participation of the cyano group.[14,44] A chainlike structure is realized in the $Cu(NCacac)_2$

---

(32) Macicek, J.; Angelova, O.; Petrov, G.; Kirilov, M. *Acta Crystallogr.* **1988**, *C44*, 626.
(33) (a) Nakashima, M.; Mikuriya, M.; Muto, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 968. (b) Corain, B.; Basato, M.; Favero, G.; Rosano, P. *Inorg. Chim. Acta* **1984**, *85*, L27. (c) Maki, A. G. *J. Chem. Phys.* **1965**, *43*, 3193.
(34) (a) Craine, G. D.; Thompson, H. W. *Trans. Faraday Soc.* **1953**, *49*, 1273. (b) Moller, C. K.; Stoicheff, B. T. *Can. J. Phys.* **1954**, *82*, 630. (c) Morino, Y.; Kuchitsu, K.; Hori, Y.; Tanimoto, M. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2349.
(35) Storhoff, B. N. *Coord. Chem. Rev.* **1977**, *23*, 1.
(36) Piper, T. S. *J. Chem. Phys.* **1961**, *35*, 1240.
(37) Fenton, N. D.; Gerloch, M. *Inorg. Chem.* **1989**, *28*, 2767.
(38) (a) Ballhausen, C. J.; Jorgensen, C. K. *Acta Chem. Scand.* **1955**, *9*, 397. (b) Reedijk, J.; Driessen, W. L.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1095.
(39) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968.
(40) Lodzinska, A.; Czerniawska, Z.; Klobukowski, M. *Pol. J. Chem.* **1979**, *53*, 1961.
(41) Gerloch, M.; Wooley, R. G. *Prog. Inorg. Chem.* **1984**, *31*, 371.
(42) Bencini, A.; Benelli, C.; Gateschi, D.; Zanchini, C. *Inorg. Chem.* **1983**, *22*, 2123.
(43) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478.

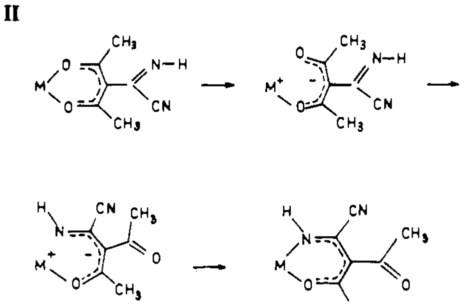
compound,[5] where just one of the two symmetrically nonequivalent ligands performs the bridging function. The cyano group from the second ligand does not approach any of the neighboring copper atoms, probably because of the operation of the Jahn–Teller effect and/or the presence of a plane-to-plane ligand stacking often met in other copper acetylacetonato complexes.[45] Joining of molecules in 2D nets has been encountered in the $Cu(NCpaac)_2$[32] complex (here NCpaac we consider as a phosphorus analogue of NCacac), where both cyano groups take part in bonding with adjacent metal centers. In the present 3D-network structure of $Co(NCacac)_2$, the lengths of the coordination bonds of the cobalt atom show a tendency toward an equalization of the inter- and intramolecular interactions. This is supported by the electronic structure of the CoO_4N_2 moiety deduced from the AOM analysis of its electronic absorption spectrum. While both nitrogen and oxygen atoms act as σ-donor ligands toward the Co(II) ion and the oxygen orbitals of π type within the chelate plane are of donor type, the orbitals of the conjugated ligand system are π acceptors, which serves as a probe for π back-bonding. Thus formed coordination bonds are equivalent and strong enough to hold the molecules in a regular but somewhat loose 3D structure. Presumably, electronic effects rather than crystal packing forces are responsible for the observed molecular ordering. The π-bonding anisotropy may explain the large symmetry reduction of the CoO_4N_2 chromophore from O_h to D_{4h} and further to D_{2h}, reflected in the solid-state ligand-field spectrum and the very low orbital contributions to the spin-only ($\mu = 3.88\ \mu_B$ for $S = {}^3/_2$[46]) magnetic moment of Co(II) ($\mu = 3.957\ \mu_B$).

It was pointed out in the Introduction that some substituents at the 3-positions in 2,4-pentanedione favor the formation of various five- or six-membered chelates, **2** and **3**. In these cases a competitive intramolecular bonding of the substituent takes place instead of the additional intermolecular linking (vide supra). Such behavior was described by Svensson et al.[9] for *N*-(2,2-diacetylvinyl)-*o*-phenylenediamine coordinated to the Co(III) ion (a type **2** complex). This ligand's hydrogen-bonded molecular self-complex[47] and some other trans-enol-stabilized 3-substituted acetylacetones[3,15g,48] obey this scheme as well. The Pd(II) complex of (1,2-bis(trifluoromethyl)ethenyl)acetylacetonate[8] also belongs to type **2** with the primary Pd–carbonyl bond replaced by a Pd–ethenyl carbon one. Type **3** chelation is realized in the Co(III)[12] and Fe(II)[11] complexes of 3-(hydroxyimino)-2,4-pentanedionate (XY = NO). An essentially planar five-membered ring is formed in the (3-diazo-2,4-pentanedionato)molybdenum complex[49] (XY = NN). Two anulated five-membered rings, one being of type **3** (X = C), were found in the product of $Fe(CO)_4$ insertion into the three-membered ring system of 1,2-diphenyl-4,4-diacetyltriafulvene.[50]

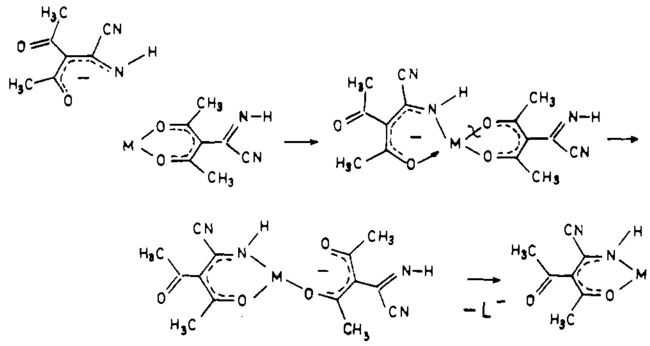
From the above examples, it appears that when the 3-substituent (XY) in an acac ligand possesses polar, electron-rich, and geometrically adequate functional group(s) the usual dicarbonyl chelate may be transformed into an alternative XY-containing ring under certain conditions. Such structural rearrangement is expected to occur in any XYacac complex if the particular ligand has sufficient conformational flexibility and the new metal-to-ligand bond interaction lowers the energy of the system. The released carbonyl group may further participate in an additional intermolecular linking to other metal centers if there are any.

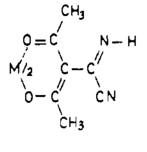
We shall apply the above formulations to reconsider the constitution of some complexes of **4** reported by Corain et al.[15] These authors have pointed out and tried to confirm by different techniques that, besides the usual complexes **6**, another species **7** of

Scheme II

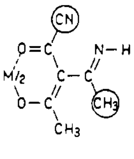


Scheme III

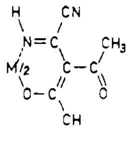




6a, M=Ni
b, M=Zn



7a, M=Ni
b, M=Cu



8

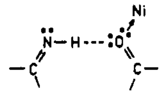
the new 1-cyano-2-(1-iminoethyl)butane-1,3-dionato ligand had been formed. **6** and **7** differed from each other only in the positions of the encircled cyano and methyl groups in the ligands. A tentative hypothesis of the water-catalyzed transformation **6a** → **7a** has been regarded to account for the structure found for **7a**.[15a] It included an isomerization of **6a** to a species of type **8** with subsequent >C=NH hydrolysis, metal-coordinated carbonyl group ammonolysis, and final formation of **7a**. This scheme, however, did not receive any confirmation later. Instead of that, we consider **8** the final product of the isomerization and **7a** its incorrect alternative, with carbonyl oxygen and imino nitrogen atoms interchanged. The **6a** → **8** conversion may follow two pathways. The first, intramolecular, involves breakage of an M–O bond, rotation around a C–C bond in the ligand, and formation of a new M–N bond (Scheme II). The alternative, intermolecular, reaction presumes subsequent coordination of the imino nitrogen and carbonyl oxygen atoms of an external ligand to the metal atom accomplished by displacing the O,O-chelated ligand (Scheme III). The idea of formation of intermediate products similar to **8** is not new. It has been employed by Uehara et al.[51a] in the explanation of the reaction mechanism of $M(acac)_2$-catalyzed (M = Mg, Co, Ni, Zn, Cu) addition of various acceptor molecules to acetylacetone although controverted by Nelson et al.[51b]

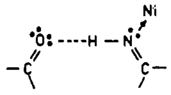
The misconception of Corain et al., in our opinion, began with the crystal structure analysis of the nickel complex[15a] and continued with that of the copper complex.[15c] The final discrepancy factors R and R_w for structures **7a**/**7b** were relatively high: 0.047/0.062 and 0.057/0.066, respectively, in contrast to the excellent quality of the X-ray experiments [PW1100 diffractometer; 1342

---

(44) Cox, M.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1965**, 2840.
(45) Aruffo, A. A.; Anderson, L. D.; Lingafelter, E. C.; Schomaker, V. *Acta Crystallogr.* **1983**, *C39*, 201.
(46) Carlin, R. L. *Transition Metal Chemistry*; Marcel Dekker: New York, 1965; Vol. 1, p 1.
(47) Svensson, C.; Ymen, I.; Yom-Tov, B. *Acta Chem. Scand., Ser. B* **1982**, *36*, 71.
(48) Dekaprilevich, M. O.; Voroncova, L. G.; Chizhov, O. S. *Izv. Akad. Nauk* SSSR, *Ser. Khim.* **1980**, 2050.
(49) Bell, L. K.; Herrmann, W. A.; Ziegler, M. L.; Pfisterer, H. *Organometallics* **1982**, *1*, 1673.
(50) Dettlaf, G.; Behrens, U.; Eicher, T.; Weiss, E. *J. Organomet. Chem.* **1978**, *152*, 197.
(51) (a) Uehara, K.; Ohashi, Y.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1447. (b) Eckberg, R. P.; Nelson, J. H.; Kenney, J. W.; Howells, P. N.; Henry, R. A. *Inorg. Chem.* **1977**, *16*, 3128.

(1127)/1320 (1097) measured (observed with $I > 2.5\sigma(I)$) reflections]. All hydrogen atoms, except that bonded to the imino nitrogen, were localized in the final difference Fourier maps and included in calculations. We used the reported[15a,c] coordinates to evaluate the nonbonding intermolecular distances around the carbonyl oxygen and imino nitrogen atoms in question. For **7a** the shortest distance of 3.045 Å was found between the two particular O and N atoms, which conformed to the C═O···H—N═C hydrogen-bond geometry. This scheme may be realized in **8** as well, assuming the O and N atoms are exchanged.[52]


9


10

In the structure of **7b**, the carbonyl oxygen has the shortest intermolecular contact with a cyano nitrogen, at 3.224 Å, and the imino nitrogen points toward two methyl groups, the N···C distances being 3.440 and 3.529 Å, respectively. A more realistic intermolecular linking scheme can be deduced for **8b**, i.e. N—H···N≡C hydrogen-bond and C═O···H_3C contacts. The reliability of the formation of a metal–imino nitrogen coordination bond in complexes of type **8** is further supported by diverse structural examples.[53]

The structural misassignments were connected with the uncertain interpretation of the IR spectral data.[15a] The stretching frequency ν_{N-H} at 3200 cm^{-1} for **7a** was reported to be close to that of the solid **4** (3270 cm^{-1}) whereas the existence of a band at 3245 cm^{-1} for **6a** was left without comment. The almost negligible difference in the intensity of the very weak $\nu_{C\equiv N}$ bands at 2220/2235 cm^{-1} for **6a**/**7a**, postulated as being due to the quenching effect of the neighboring oxygen atom in **7a**, can be alternatively explained in terms of the cyano group conjugation with the imino C═N π system perturbed upon coordination, as in **8**.

Finally, the pronounced preference of zinc for oxygen-bearing ligands would make probable the formation of two isomers—**6b** and **7**—if the ligand constitution in **7** were correct. However, the existence of only **6b** was reported.[15d,i]

Conclusions

The above discussion demonstrates in a qualitative manner than the coordination modes of acetylacetonato ligands 3-substituted by polar group(s) are subject to alteration depending on the flexibility and rotation freedom of the ligands themselves, the metal–donor group compliance, and the relative stability of the possible chelates. The conception of ligation competition between the actively coordinating donor groups allows us to suggest an alternative molecular configuration of complexes **7**. 3-(Cyanoiminomethyl)acetylacetone, known for more than 80 years,[15a] is shown to be able to coordinate through the imino nitrogen atom to metal ions preferring N-donor ligands. Two schemes are developed to explain how this could be accomplished.

The 3-cyano-2,4-pentanedionato ligand is not stereochemically allowed to under such changes in its chelation mode but is rigorously forced to act as a bridging ligand. The visible and near-IR electronic spectra of this system and the very low orbital contributions to the observed magnetic moment can be explained only by a very large ground-state splitting of a π type that characterizes the NCacac ligand as an in-plane π donor and an out-of-plane π acceptor. The structure of the $Co(NCacac)_2$ complex is a remarkable example of 3D regular molecular ordering with well-balanced metal–metal distances. The spectral and magnetic data reveal some π back-bonding on the electronic levels of the conjugated chelate system, which could be responsible for the equalization of the intra- and intermolecular interactions.

Acknowledgment. O.A. is grateful to the Bulgarian Ministry of Education for a Ph.D. grant. We thank Dr. Zecheva from the Institute of General and Inorganic Chemistry for the magnetic susceptibility measurements.

Supplementary Material Available: Tables SI and SIII, listing non hydrogen atom anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and AOM expressions for the non-zero matrix elements of the ligand-field and the quartet-state matrices for a *trans*-MO_4N_2 chromophore (2 pages); Table SII, listing observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

---

[52] The closeness of the X-ray scattering power of O and N is often compensated by their temperature factors in the least-squares refinements.

[53] (a) Hollian, B. L.; Marsh, R. E. *Acta Crystallogr.* **1970**, *B26*, 1049. (b) Matthew, M.; Kunchur, N. R. *Acta Crystallogr.* **1970**, *B26*, 1054. (c) Coghi, L.; Pelizzi, G. *Acta Crystallogr.* **1975**, *B31*, 131. (d) Birker, P. J. M. W. L. *J. Chem. Soc., Chem. Commun.* **1977**, 444. (e) Peng, S.-M.; Wang, Y.; Chiang, C.-K. *Acta Crystallogr.* **1984**, *C40*, 1541.

Notes

Contribution from the Department of Chemistry,
Box CH, Mississippi State University,
Mississippi State, Mississippi 39762

Facile α/β Diastereomerism in Organocobalt Corrins. Generality of the Phenomenon and Characterization of Additional α-Diastereomers

Kenneth L. Brown,* Xiang Zou, and Laurent Salmon

Received September 28, 1990

Introduction

In a recent publication,[1] we reported that reductive alkylation of cobinamides (Cbi's) with CF_3CH_2I resulted in formation of a mixture of diastereomeric (2,2,2-trifluoroethyl)cobinamides with the α-diastereomer (i.e. the organic ligand in the "lower" axial position) predominating over the β-diastereomer by about 7-fold. This surprising result was in stark contrast to earlier work,[2] which had shown that reductive alkylation of cobinamide with $^{13}CH_3I$ yielded a methylcobinamide product that was at least 95% β-diastereomer. We now report the results of a reexamination of the products of reductive alkylation of cobinamide and cobalamin with CH_3I, as well as the products formed with a variety of other alkylating agents. These results show that formation of pairs of diastereomeric α- and β-alkylcobinamides is a general phenomenon and that similar pairs of diastereomeric α- and β-alkylcobalamins can also be obtained under some conditions.

Experimental Section

Alkylating agents and aquocobalamin (H_2OCbl) were obtained commercially. Factor B[3] was prepared as described previously.[4,5] HPLC was performed with a 4.6 × 75 mm Beckman C_{18} Ultrasphere column using a 50 mM aqueous ammonium phosphate buffer, pH 3.0 (solvent A), and acetonitrile (solvent B).[6] The gradient used was 5% B for 2 min

---

[1] Brown, K. L.; Evans, D. R. *Inorg. Chem.* **1990**, *29*, 2559–2561.

[2] Brown, K. L.; Peck-Siler, S. *Inorg. Chem.* **1988**, *27*, 3548–3555.

[3] Factor B is a mixture of the diastereomers of cyanoaquocobinamide, α-CN-β-(H_2O)Cbi and α-H_2O-β-(CN)Cbi.

[4] Renz, P. *Methods Enzymol.* **1971**, *18*, 82–92.

[5] Brown, K. L.; Hakimi, J. M.; Nuss, D. M.; Montejano, Y. D.; Jacobsen, D. W. *Inorg. Chem.* **1984**, *23*, 1463–1471.

[6] Jacobsen, D. W.; Green, R.; Brown, K. L. *Methods Enzymol.* **1986**, *123*, 14–22.