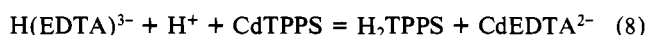


gives strong evidence for pK_{a1} , while there is disagreement as to the magnitude of this pK_a or even the existence of pK_{a2} in this system due to the minor absorbance variations found.^{17,21,22} Our kinetically determined pK_{a2} s of $Gd^{III}TPPS$ (7.5 and 9.2) are similar²¹ to those of $Co^{III}TPPS$ (7.02 and 9.76) and other trivalent porphyrins. It has been noted that the ligand TPPS has more influence on pK_{a1} than does the identity of the metal ion itself.²³ In agreement with Srivastava,⁹ no evidence for $GdTPPS$ self-association was found.

Solutions containing 10 μM metalloporphyrin and 25 mM EDTA at pH 8 were allowed to stand overnight in the dark. The Ni(II), Mn(III), Cu(II), Rh(III), In(III), Zn(II), Co(III), $V^{IV}O$, Fe(III), Al(III), Cr(III), and Sn(IV) complexes of TPPS were not demetalated. Pd(TMPyP) [TMPyP = tetrakis(1-methylpyridium-4-yl)porphyrin] was photoreduced in dim light in the presence of EDTA to the palladium chlorin.²⁴ As expected, the labile CdTPPS was demetalated, since the equilibrium constant²⁵ for reaction 8 is ca. 10^{16} . It appears that the weak metal to



porphyrin bonding of the large Gd^{3+} ion in $GdTPPS$ favors metal removal by EDTA.

In the reaction of $FeEDTA^{2-}$ with cobalt(III) porphyrins,²⁶ the rate law indicated that a complex formed between the negatively charged reductant and positively charged porphyrin. No evidence for such complexation was found with negatively charged metalloporphyrins, and such is the case in the present study where both reactants are negatively charged.

The area of metal exchange between two ligands has been reviewed²⁷ and much of this work involves EDTA chelates. Postulation of initial solvent displacement from the metal ion followed by EDTA oxygen atom coordination with subsequent chelation-dechelation steps in the mixed complex is applicable both to classical complexes and to the $GdTPPS/EDTA$ reaction. Our data indicate that $H(EDTA)^{3-}$ is substantially more reactive than both $H_2(EDTA)^{2-}$ and $EDTA^{4-}$, and the protonated forms of EDTA generally exhibit differing reactivities, where the relative contributions of each depend on the nature of the substrate.²⁷ The rate constants of $H(EDTA)^{3-}$ with $HO(H_2O)_3GdP^-$ and $(H_2O)_4GdP$ and are in the ratio of 36:1, and the same trend is found in certain anation reactions of cobalt(III)-porphyrins. With $Co^{III}TPPS$ and SCN^- , the diaquo to monohydroxy ratio²⁸ is 4.2:1, whereas with CN^- , the ratio²⁰ is 7.7:1. For Gd^{III} , Rh^{III} , and $Co^{III}TPPS$ [also $Co^{III}TMPyP^{28}$], the dihydroxy forms are at least several orders of magnitude less reactive as compared to species containing at least one coordinated water molecule. The cobalt(III) porphyrin reactions are considered dissociative in character^{21,28,29} where the coordinated hydroxide labilizes a water molecule, facilitating dissociation to provide a position for the entering ligand. Thus, the $GdTPPS/EDTA$ reaction also appears dissociative, with a rate determining step similar to that of simpler monoanions.

Work is in progress with other water-soluble lanthanide porphyrins. It is noted that the reactive $HO(H_2O)_3GdTPPS^-$ is in high concentration at pH 7.5. The fact that $GdTPPS$ (but not $Mn^{III}TPPS$) was demetalated² when equilibrated for several days

with human plasma at this pH could be due to a biological chelating agent acting in a manner similar to EDTA.

Acknowledgment. This work was supported by Howard University NIH Biomedical Research Grant 5-SO-6-RR-08019-9.

Registry No. EDTA, 60-00-4; $GdTPPS$, 107283-78-3.

Supplementary Material Available: Table I, giving pH, [EDTA], and observed and calculated $k_{obsd}/[EDTA]$ values (1 page). Ordering information is given on any current masthead page.

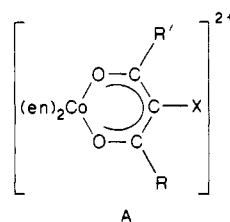
Contribution from the Department of Chemistry, University of Miami, Coral Gables, Florida 33124, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2, and Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1H 5W1

Use of Extended Hückel Molecular Orbital Calculations in Determining the Position of Attack in Inner-Sphere Electron-Transfer Reactions: X-ray Crystal Structure of (1,3-Diphenylpropane-1,3-dionato)bis(ethylenediamine)cobalt(III)

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Received August 6, 1987

We have synthesized and studied the redox chemistry of a number of bis(ethylenediamine)cobalt(III) complexes of β -diketones having the general formula given in A where $R = R' =$



CH_3 and $X = H, CHO, COCH_3, Cl, Br,$ and I ; $R = CH_3, R' = H,$ and $X = COCH_3$; $R = R' = C_6H_5$ and $X = H$. With the exception of the last complex, all of these were thought to involve at least partial inner-sphere attack of the reductant, Cr(II), either at the coordinated oxygen or at the X substituent.¹⁻³

The presence of phenyl substituents on the β -diketone ring resulted in a complex having very peculiar reduction properties. The most noticeable effect was that the reaction with Cr(II) was autocatalytic and was inversely related to the acidity of the medium.⁴ Further, the perchlorate salt of A crystallized from triply distilled water always contained an extra $HClO_4$ upon analysis. The location of this additional proton was of interest considering the inverse acid dependency observed in the kinetics. The perchlorate crystals were thin plates that were unsuitable for a crystal study. After several other counterions were tried, a suitable crystal was grown in a neutral nitrate medium. The crystals were rectangular and the structure, reported in this work, indicated that the complex was unprotonated. If the crystals were grown in nitric acid, they formed long needles initially, which were crystallographically identical with the rectangular crystals obtained from neutral solutions. After some time, thin plates began to appear in the acidic nitrate medium. These were by analysis also a protonated form of the complex but as was true when the counterion was perchlorate, they were unsuitable for X-ray analysis.

- (21) Ashley, K. R.; Au-Young, S. *Inorg. Chem.* **1976**, *15*, 1937.
 (22) Krishnamurthy, M. *Inorg. Chim. Acta* **1977**, *25*, 215.
 (23) El-Awady, A. A.; Wilkins, P. C.; Wilkins, R. G. *Inorg. Chem.* **1985**, *4*, 2053.
 (24) Richoux, M. C.; Neta, P.; Harriman, A.; Baral, S.; Hambright, P. J. *Phys. Chem.* **1986**, *90*, 2462.
 (25) The formation constant of $Cd(EDTA)^{2-}$ is $\log K = 16.4$ (Sarma, B. D.; Ray, P. J. *Indian Chem. Soc.* **1956**, *33*, 841) and the equilibrium constant for the $H_2P + Cd^{2+} = CdP + 2H^+$ reaction has $\log K = ca. 10$ (Shamim, A.; Hambright, P. *Inorg. Chem.* **1980**, *19*, 564).
 (26) Langley, R.; Hambright, P. *Inorg. Chem.* **1985**, *24*, 3716.
 (27) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martel, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; Vol. 2, Chapter 1.
 (28) Ashley, K. R.; Leipoldt, J. G. *Inorg. Chem.* **1981**, *20*, 2326.
 (29) Pasternack, R. F.; Cobb, M. A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4327.

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To the best of our knowledge, this is only the second structure to be solved for this ligand attached to cobalt(III), the first being the (dibenzoylmethano)[*N,N'*-*o*-phenylenebis(salicylaldehyde-*o*-iminato)]cobalt(III) complex reported by Cummins et al.⁵ in 1976. The free ligand, dibenzoylmethane or 1,3-diphenylpropane-1,3-dione, exists in the solid state and the X-ray crystal structure of this material has been determined.⁶⁻⁸ Other metal complexes incorporating this ligand that have been structurally determined by X-ray diffractometry include those with the metals tin,^{9,10} niobium,^{11,12} manganese,¹³ uranium,^{14-16,28} rhenium,¹⁷ copper,¹⁸⁻²⁰ iron,²¹ manganese,²² calcium,²³ strontium,²⁴ zirconium,²⁵ nickel,²⁶ palladium,²⁷ and cerium.^{16,28}

Experimental Section

Reagents. All reagent solutions were prepared, standardized, and handled as described previously.²⁹

Preparations. (1,3-Diphenylpropane-1,3-dionato)bis(ethylenediamine)cobalt(III) Perchlorate, [Co(en)₂(dppd)](ClO₄)₂. Triethyl phosphate (80 mL) was dried over molecular sieves overnight before adding NOBF₄ (2.78 g). The complex *cis*-[Co(en)₂(N₃)₂](ClO₄)³⁰ (4.36 g) was added in several portions. When evolution of gases ceased, the ligand 1,3-diphenylpropane-1,3-dione (dibenzoylmethane, 2.69 g, Aldrich Chemical Co., Inc.) was introduced into the reaction mixture. The solution was heated on a steam bath for 60 h with occasional swirling. Precipitation was effected by pouring slowly the cooled reaction mixture into a beaker containing diethyl ether (4 L), which was vigorously being stirred. The resulting solid was dissolved in water and was ion-exchanged on CM-Sephadex C-25-120 (Sigma Chemical Co.). The eluent was an aqueous solution of NaCl (0.1–0.2 M). After the desired orange band was moved away from the other bands on the column, it was physically removed and was placed on a smaller column. The complex was liberated

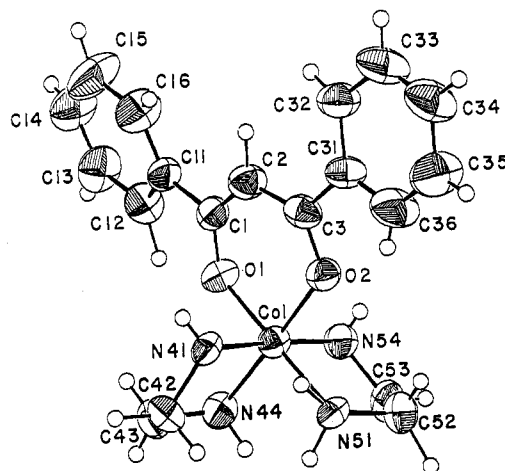


Figure 1. ORTEP plot of (1,3-diphenylpropane-1,3-dionato)bis(ethylenediamine)cobalt(III).

Table I. Fractional Atomic Coordinates

atom	x/a	y/b	z/c
Co1	0.2454 (1)	0.0857 (1)	0.9646 (1)
O1	0.2693 (3)	0.1243 (1)	0.0976 (6)
C1	0.2202 (6)	0.3445 (2)	0.6080 (10)
C2	0.1558 (7)	0.3327 (3)	0.5090 (10)
C3	0.1415 (6)	0.3506 (3)	0.3769 (10)
O2	0.1778 (4)	0.3824 (2)	0.3416 (6)
C11	0.2427 (7)	0.1776 (2)	0.2392 (10)
C12	0.2979 (9)	0.1620 (4)	0.3393 (13)
C13	0.3208 (10)	0.1815 (4)	0.4616 (14)
C14	0.2878 (9)	0.2180 (3)	0.4823 (14)
C15	0.2345 (10)	0.2345 (4)	0.3827 (13)
C16	0.2094 (7)	0.2146 (3)	0.2590 (13)
C31	0.0849 (6)	0.3320 (2)	0.2645 (11)
C32	0.0246 (8)	0.3012 (3)	0.2880 (13)
C33	-0.0283 (10)	0.2856 (5)	0.1820 (18)
C34	-0.0237 (9)	0.3001 (4)	0.0488 (16)
C35	0.0369 (8)	0.3300 (3)	0.0185 (11)
C36	0.0905 (7)	0.3464 (3)	0.1249 (11)
N41	0.3598 (5)	0.0981 (2)	-0.1343 (9)
C42	0.4330 (7)	0.0702 (3)	-0.0921 (12)
C43	0.4220 (7)	0.0625 (3)	0.0612 (11)
N44	0.3219 (5)	0.0530 (2)	0.0881 (8)
N51	0.2152 (5)	0.0455 (2)	-0.1669 (9)
C52	0.1188 (7)	0.0314 (3)	-0.1380 (11)
C53	0.1060 (7)	0.0320 (3)	0.0179 (10)
N54	0.1337 (5)	0.0709 (2)	0.0669 (8)
N7	0.1021 (6)	-0.0802 (2)	0.0066 (8)
O71	0.0945 (5)	-0.0709 (2)	-0.1205 (7)
O72	0.0451 (4)	-0.1022 (2)	0.0604 (8)
O73	0.1651 (6)	-0.0676 (3)	0.0765 (8)
N8	0.3428 (5)	-0.0456 (2)	-0.0745 (9)
O81	0.3593 (4)	-0.0799 (2)	-0.0992 (7)
O82	0.3546 (4)	-0.0314 (2)	0.0442 (6)
O83	0.3155 (5)	-0.0255 (2)	-0.1747 (7)

from the resin by passing a saturated solution of NaCl through the second column, and the orange product was finally precipitated by the addition of solid NaClO₄. This complex has been prepared by an alternative method as the iodide salt.³⁰ Anal. Calcd for [Co(C₂H₈N₂)₂(C₁₅H₁₀O₂)](ClO₄)₂·HClO₄: C, 32.52; H, 4.02; N, 7.98. Found: C, 32.10; H, 3.92; N, 7.90. UV-vis λ_{max}, nm (ε_{max}, M⁻¹ cm⁻¹): 488 (171 ± 1), 372 (10 900 ± 100), 300 (14 700 ± 100), 263 (24 500 ± 200).

[Cr(OH)₂(dppd)]⁺ by Electron Transfer. The product of the electron-transfer reaction between [Co(en)₂(dppd)]²⁺ and Cr(II) was a yellow compound, which could be isolated in pure form by very rapid ion-exchange on SP-Sephadex (SP-25-120) resin. Elution with 0.1 M NaCl afforded a yellow solution with the yellow band decomposing to an intractable and highly charged green material on the column. The concentration of chromium in the eluted yellow band (which was very stable once removed from the column) was determined by analyzing the chromium as chromate.³¹ UV-vis λ_{max}, nm (ε_{max}, M⁻¹ cm⁻¹): 570 (27),

- Balahura, R. J.; Lewis, N. A. *Can. J. Chem.* **1975**, *53*, 1154.
- Balahura, R. J.; Lewis, N. A. *Can. J. Chem.* **1979**, *57*, 1765.
- Balahura, R. J.; Lewis, N. A., submitted for publication in *Inorg. Chim. Acta*.
- Balahura, R. J.; Lewis, N. A. *Inorg. Chim. Acta* **1987**, *130*, 151.
- Cummins, D.; McKenzie, E. D.; Milburn, H. *J. Chem. Soc., Dalton Trans.* **1976**, 130.
- Williams, D. E. *Acta Crystallogr.* **1966**, *21*, 340.
- Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1552.
- Jones, R. D. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1807.
- Uchida, T.; Kozawa, K.; Obara, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3227.
- Bancroft, G. M.; Davies, B. W.; Payne, N. C.; Sham, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 973.
- Dahan, F.; Kergoat, R.; Senechal-Tocquer, M.-C.; Guerschais, J. E. *J. Chem. Soc., Dalton Trans.* **1976**, 2202.
- Dahan, F.; Kergoat, R.; Senechal-Tocquer, M.-C.; Guerschais, J. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1038.
- Cornwall, A. B.; Harrison, P. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1694.
- Graziani, R.; Marangoni, G.; Paolucci, G.; Forsellini, E. *J. Chem. Soc. Dalton Trans.* **1978**, 818.
- Charpin, P.; Lance, M.; Soulie, E.; Vigner, D.; Naraza, A. *Eur. Crystallogr. Meet.* **1982**, *1*, 213.
- Kepert, D. L.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 567.
- Barrick, J. C.; Fredette, M.; Lock, C. J. L. *Can. J. Chem.* **1973**, *51*, 317.
- Blackstone, M.; van Thuijl, J.; Romers, C. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 557.
- Knyazeva, A. N.; Shugam, E. A.; Shkol'nikova, L. M. *Zh. Strukt. Khim.* **1969**, *10*, 83.
- Addison, A. W.; Burke, P. J.; Henrick, K. *Inorg. Chem.* **1982**, *21*, 60.
- Kaitner, B.; Kamenar B. *Cryst. Struct. Commun.* **1980**, *9*, 487.
- Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1289.
- Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1295.
- Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1303.
- Chum, H. K.; Steffen, W. L.; Fay, R. C. *Inorg. Chem.* **1979**, *18*, 2458.
- Kasumov, V. T.; Gusejnova, M. K.; Medzhidov, A. A.; Mamedov, Kh. S. *Zh. Strukt. Khim.* **1981**, *22*, 90.
- Shugam, E. A.; Shkol'nikova, L. M.; Knyazeva, A. N. *Zh. Strukt. Khim.* **1968**, *9*, 222.
- Kepert, D. L.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 567.
- Lewis, N. A.; Ray, A. M. *Inorg. Chem.* **1985**, *24*, 340.
- York, R. J.; Bonds, W. D. Jr.; Cotsoradis, B. P.; Archer, R. D. *Inorg. Chem.* **1969**, *8*, 789.

- Kothari, V. M.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 2276.

480 (240), 458 (290), 378 (14 000), 286 (11 000).

[Cr(OH₂)₂(dppd)]⁺ by Substitution. A 50% aqueous acetone solution (20 mL) containing 1.2 g of chromium(III) perchlorate (G. Frederick Smith) and 1.2 g of dibenzoylmethane (Aldrich) was allowed to react for 2 weeks. Ion exchange of a portion of this mixture revealed that a small amount of [Cr(OH₂)₅(dppd)]⁺ had formed with spectral parameters identical with those of the complex formed by electron transfer. It also decomposed quickly to the green material on the column.

Crystal Data. CoC₁₉H₂₇N₄O₂(NO₃)₂; *M_r* = 526.40, orthorhombic, space group *Pbca*, *a* = 14.263 (2) Å, *b* = 34.781 (7) Å, *c* = 9.375 (1) Å, *V* = 4651 (2) Å³, *Z* = 8, *D_{calcd}* = 1.50 Mg m⁻³, *F*(000) = 2192, *μ* = 0.76 mm⁻¹, λ(Mo-Kα) = 0.71073 Å, crystal size = 0.20 × 0.15 × 0.30 mm.

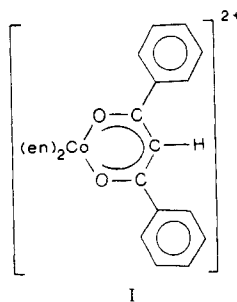
Preliminary precession photographs of a suitable crystal were used to determine the space group and approximate cell dimensions. The crystal was then mounted on a Picker FACS-I diffractometer equipped with graphite-monochromated Mo Kα radiation. Cell dimensions and an orientation matrix were obtained from a least-squares fit to the coordinates of 12 Friedel pairs of centered reflections with 2θ ≥ 35°. Intensity data were collected for 5° ≤ 2 ≤ 45° by using an ω-2θ scan at a rate of 2° (2θ) min⁻¹. Background levels were estimated from standing counts of one-tenth of the scan time at each end of a scan. If the reflection had a significant intensity [*I* ≥ 2σ(*I*)] the profile of the peak was analyzed to provide an improved estimate of the background. Three standard deviations, monitored every 100 reflections throughout the data collection, showed no significant deviations from their mean values. The intensities of 3007 unique reflections were measured, of which 1682 were considered observed (*I* ≥ 3σ(*I*)) and included in subsequent calculations. The structure was solved by using the MULTAN-80³² direct-methods routines and refined by least-squares techniques minimizing the function Σw(|*F_o*| - |*F_c*|)². The weighting scheme was of the form *w* = 1/(σ|*F*|² - *p*|*F_c*|²) where σ(*F*) was derived from counter statistics and a value of *p* = 0.005 was determined from the standards. The hydrogen positions were determined from a difference synthesis and were included in the final cycles of refinement with isotropic thermal parameters. The final residuals were *R* = (Σ|Δ*F*|/Σ|*F*|) = 0.063 and *R'* = (ΣwΔ|*F*|²/Σw|*F*|²) = 0.062, 10.074, and 0.072, respectively, including unobserved reflections. A final difference synthesis showed no abnormal features with a maximum peak height of 0.96 e/A³ in the vicinity of Co1. Scattering factors were taken from ref 33 and were corrected for anomalous dispersion. The program used was SHELX-76.³⁴ The cation is shown in Figure 1, coordinates of the non-hydrogen atoms are given in Table I, and Table II contains the bond distances and angles.

Molecular Orbital Calculations. An extended Hückel program developed by Dr. M. Zerner and modified by Dr. F. Grein was employed. The input was idealized crystallographic data giving *C_{2v}* symmetry. Ten cycles were allowed in each run, but convergence was always reached before this value was attained.

Instrumentation. The visible spectra were run on a Perkin-Elmer Model 330 UV-vis-near-IR spectrophotometer. The crystal structure was solved on a WICAT System 150 WS microcomputer and the molecular orbital calculations were performed on an IBM 3082 mainframe computer.

Results and Discussion

Our interest in this work was kindled by our attempts to study the redox reaction between [Co(en)₂(dppd)]²⁺ (compound I where



(32) Main, P.; Fiske, S. J.; Hall, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. L. "Multan 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, 1980.

(33) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1973; Vol. IV.

(34) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination"; Cambridge University, 1976.

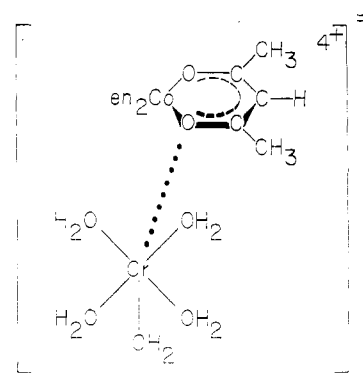


Figure 2. Position of attack of Cr(II) on pentane-2,4-dione type complexes of cobalt(III).

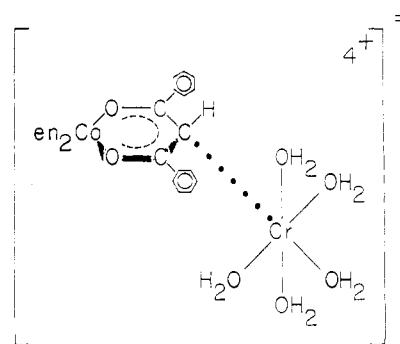
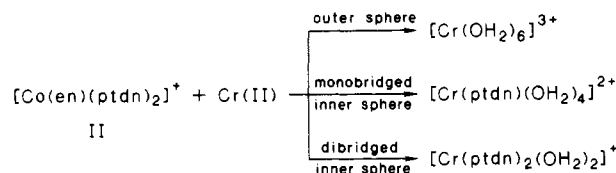


Figure 3. Position of attack of Cr(II) on the 1,3-diphenylpropane-1,3-dione complex of cobalt(III).

en = ethylenediamine and dppd = 1,3-diphenylpropane-1,3-dionato) and Cr(II). Earlier studies^{35,36} on related β-diketone metal complexes showed that multiple redox pathways were possible and one species, [Co(en)(ptdn)]⁺ (compound II, where ptdn = pentane-2,4-dione) exhibited an outer-sphere pathway giving [Cr(OH₂)₆]³⁺ as the reductant product, as well as two inner-sphere pathways simultaneously.



One inner-sphere attack occurred at the oxygen of the ptdn ring (Figure 2). This, followed by rapid ring closure, gave the product [Cr(ptdn)(OH₂)₄]²⁺. A dibridged inner-sphere process was also observed in which the incoming reductant, Cr(II), attacked the oxygen atoms of different ptdn rings to give the [Co(ptdn)₂(OH₂)₂]⁺ product.

The next question that we wished to address, then, was how the replacement of the methyl groups on the carbon attached to the oxygen of the ptdn ligand by very electron-withdrawing substituents such as phenyl rings, would affect the inner-sphere/outer-sphere ratio of electron transfer. Much to our surprise, the mechanism of reduction of I was entirely different, with attack of the chromium(II) occurring at the central carbon atom to yield the carbon-bonded chromium(III) product (Figure 3). This reaction was a multistep process involving an auto-catalytic step and a hydrogen ion dependence. A typical scan run is shown in Figure 4. A lag period ranging from 3 to 20 min depending directly on the concentration of Cr(II) present always occurs. There are two and sometimes three isobestic points. The first two are at 504 and 575 nm and the last one occurs between

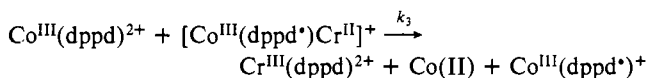
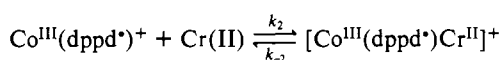
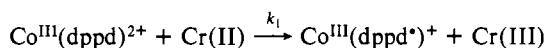
(35) Balahura, R. J.; Lewis, N. A. *J. Chem. Soc., Chem. Commun.* **1976**, 268.

(36) Balahura, R. J.; Lewis, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 4716.

Table II. Bond Distances (Å) and Angles (deg), with Estimated Standard Deviations in Parentheses

O1-Co1	1.866 (5)	C32-C31	1.390 (15)
N41-Co1	1.927 (8)	C36-C31	1.404 (14)
N44-Co1	1.956 (7)	C33-C32	1.361 (20)
N51-Co1	1.912 (8)	C34-C33	1.348 (23)
N54-Co1	1.930 (7)	C35-C34	1.382 (17)
O2-Co1	1.869 (5)	C36-C35	1.380 (15)
C1-O1	1.295 (10)	C42-N41	1.482 (13)
C2-C1	1.369 (13)	C43-C42	1.470 (15)
C11-C1	1.485 (13)	N44-C43	1.487 (12)
C3-C2	1.402 (13)	C52-N51	1.485 (13)
O2-C3	1.265 (10)	C53-C52	1.473 (14)
C31-C3	1.477 (13)	N54-C53	1.481 (11)
C12-C11	1.339 (16)	O71-N7	1.240 (10)
C16-C11	1.385 (14)	O72-N7	1.224 (11)
C13-C12	1.371 (18)	O73-N7	1.196 (11)
C14-C13	1.369 (18)	O81-N8	1.238 (11)
C15-C14	1.332 (18)	O82-N8	1.229 (10)
C16-C15	1.397 (17)	O83-N8	1.236 (10)
N41-Co1-O1	90.2 (3)	C36-C31-C3	118.5 (8)
N44-Co1-O1	85.5 (3)	C36-C31-C32	117.3 (9)
N44-Co1-N41	86.7 (3)	C33-C32-C31	122.3 (12)
N51-Co1-O1	177.2 (3)	C34-C33-C32	120.1 (14)
N51-Co1-N41	92.6 (3)	C35-C34-C33	120.1 (13)
N51-Co1-N44	94.7 (3)	C36-C35-C34	120.7 (11)
N54-Co1-O1	90.6 (3)	C35-C36-C31	119.6 (9)
N54-Co1-N41	177.2 (3)	C42-N41-Co1	108.7 (6)
N54-Co1-N44	90.6 (3)	C43-C42-N41	107.8 (8)
N54-Co1-N51	86.6 (3)	N44-C43-C42	108.0 (8)
C3-C2-C1	124.2 (9)	C43-N44-Co1	107.8 (6)
O2-C3-C2	124.1 (8)	C52-N51-Co1	109.3 (6)
C31-C3-C2	121.0 (8)	C53-C52-N51	106.9 (8)
C31-C3-O2	114.8 (8)	N54-C53-C52	106.7 (8)
C16-C11-C12	118.9 (10)	C53-N54-Co1	108.0 (5)
C13-C12-C11	121.8 (12)	O72-N7-O71	120.1 (8)
C14-C13-C12	119.7 (13)	O73-N7-O71	119.8 (8)
C15-C14-C13	119.7 (12)	O73-N7-O72	120.2 (8)
C16-C15-C14	121.0 (12)	O82-N8-O81	122.1 (8)
C15-C16-C11	118.9 (10)	O83-N8-O81	117.7 (8)
C32-C31-C3	124.2 (9)	O83-N8-O82	120.2 (8)

660 and 670 nm depending upon the concentrations of [Cr(II)] and [H⁺]. We propose the following mechanism at constant acidity:



This mechanism satisfies the observation that addition of free ligand does not accelerate the reaction nor does free ligand react with [Cr(OH₂)₆]³⁺ within the time frame of this experiment (even in the presence of Cr(II)). The active catalyst appears to be the Co(III) radical ion, which is expected to have considerable stability because of the extensive π-system in the dppd ligand. The inverse acid dependence may result from a deprotonated redox active species arising from Co^{III}(dppd⁺)⁺ or [Co^{III}(dppd⁺)Cr^{II}]⁺. We are unable to obtain sufficient information to resolve this point.

The rate law derived from this mechanism is

$$\text{rate} = k_1[\text{Co}(\text{dppd})^{2+}][\text{Cr}(\text{II})] + \frac{k_3 k_2 [\text{Co}(\text{dppd})^{2+}][\text{Cr}(\text{II})][\text{Co}(\text{dppd}^*)^+]}{k_2 + k_3[\text{Co}(\text{dppd})^{2+}]}$$

We were able to estimate only the value of $k_1 = (5 \pm 1) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C from a computer fit to the observed kinetic runs at 460 nm.

A comparison of the crystal structure of compound I containing the 1,3-diphenylpropane-1,3-dionato (dppd) ligand with the structure of a cobalt(III) compound incorporating the pentane-2,4-dionato (ptdn) ligand shows that there are no unusual features

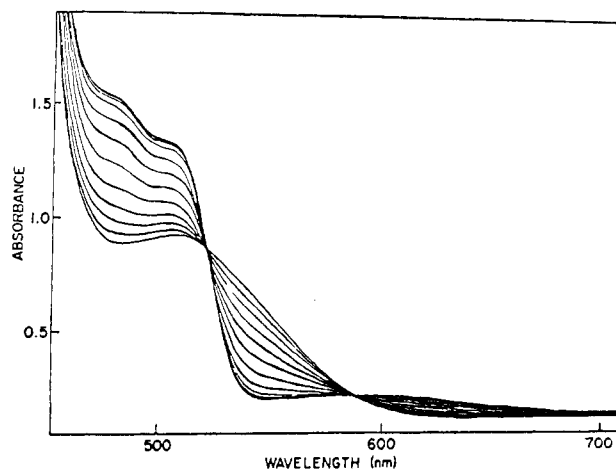


Figure 4. Typical scan run for the chromium(II) reduction of (1,3-diphenylpropane-1,3-dionato)bis(ethylenediamine)cobalt(III). Initial concentrations of reactions are [Co(en)₂(dppd)]²⁺ = 4.19 × 10⁻³, [Cr(II)] = 1.68 × 10⁻², and [H⁺] = 0.055. Temperature = 25 °C. Spectral scans were started at 0.33, 3.33, 6.33, 9.33, 12.33, 15.33, 18.33, 21.33, 24.33, 27.33, 30.33, 33.33, and 36.33 min after mixing. The last two show essentially no change.

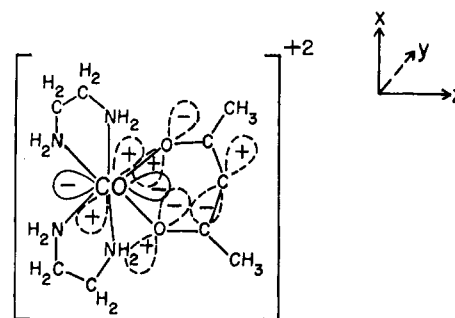


Figure 5. Important atomic orbitals in the HOMO of a pentane-2,4-dione complex of cobalt(III).

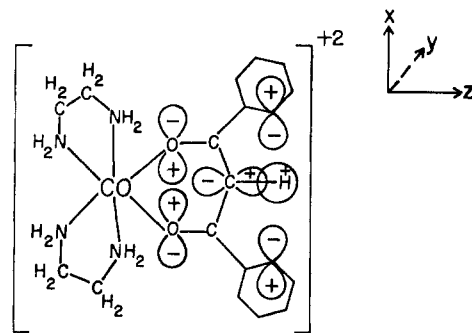


Figure 6. Important atomic orbitals in the HOMO of a 1,3-diphenylpropane-1,3-dione complex of cobalt(III).

in either molecule. The average Co–O bond distance is 1.868 Å in the dppd complex and 1.888 Å in the ptdn species. The O–Co–O “bite” angle is 94.5° in the former case and 96.5° in the latter. In both molecules, approach of the reductant to either the oxygens or to the methine carbon of the pseudoaromatic ring does not appear to be hindered. Thus, there are apparently no compelling steric reasons for the startling change in mechanism.

This leaves the possibility that the molecules may differ dramatically in their electronic properties. To test this hypothesis, both were subjected to a molecular orbital calculation using an extended Hückel program. The HOMO, in the case of the ptdn molecule, is shown in Figure 5. The maximum electron density is concentrated in the lone pairs on the oxygen atoms (68%) with 7% being located in the Co d_{yz} orbital and 21% on the methine carbon. Conversely, the HOMO of the dppd complex, illustrated in Figure 6, shows that the maximum electron density for this

molecular orbital is located on the methine carbon-hydrogen bond (41%).

Indeed, this molecular orbital has little metal character (4% of the total electron density is concentrated in the cobalt $d_{x^2-y^2}$ orbital). The oxygen atoms contain 12% of the electron density in p_x orbitals and only 6% in the oxygen lone pairs (p_y orbitals). The benzene rings account for a further 29% of the total electron density in the HOMO with all of it concentrated in the C-H linkages closest to the methine C-H bond. Thus, the reductant is drawn into a cavity of electron density (70% of the total in this molecular orbital) in the region of the methine carbon to form the precursor complex.

The energy for the HOMO of the $[\text{Co}(\text{en})_2(\text{dppd})]^{2+}$ complex is $-1066 \text{ kJ mol}^{-1}$ and that of the $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$ complex is very similar at $-1127 \text{ kJ mol}^{-1}$. The rate constant for the reduction of $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$ by $\text{Cr}(\text{II})$ is exceedingly slow ($5.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 50°C).³⁵ The corresponding reduction of $[\text{Co}(\text{en})_2(\text{dppd})]^{2+}$ is characterized by a complex mechanism, but the rate is at least 8000 times faster than that of $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$. Thus, two such very different rates with orbitals of so similar energy suggests that the mechanism of reduction must be quite different for the two compounds.

It appears from this study that there are no obvious structural differences that could account for the striking dissimilarities in the redox properties exhibited by the two closely related β -diketone complexes. The molecular orbital calculations indicate that the position of attack of the reductant to form a precursor complex is determined by the location of the maximum electron density in the HOMO. Usually, that would be expected to lie on the lone pairs of the coordinating oxygen atoms but in the case of the dppd complex, the strongly electron-withdrawing nature of the benzene rings shifts this density onto the central carbon atom. Further structural and molecular orbital studies are in progress to determine if these observations are general features of inner-sphere redox processes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for operating grants that made this work possible. Financial support from the Department of Chemistry, University of Miami, is also gratefully acknowledged. We wish to express our appreciation to Dr. F. Grein and Dr. M. Zerner for providing the molecular orbital program.

Registry No. $[\text{Co}(\text{en})_2(\text{dppd})](\text{ClO}_4)_2$, 113774-77-9; $[\text{Co}(\text{en})_2(\text{N}_3)_2](\text{ClO}_4)_2$, 14877-87-3; $[\text{Cr}(\text{OH}_2)_5(\text{dppd})]^+$, 113705-88-7; $[\text{Cr}(\text{OH}_2)_6]^{2+}$, 20574-26-9; $[\text{Co}(\text{en})_2(\text{dppd})](\text{NO}_3)_2$, 113774-78-0; $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$, 33570-80-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom parameters (2 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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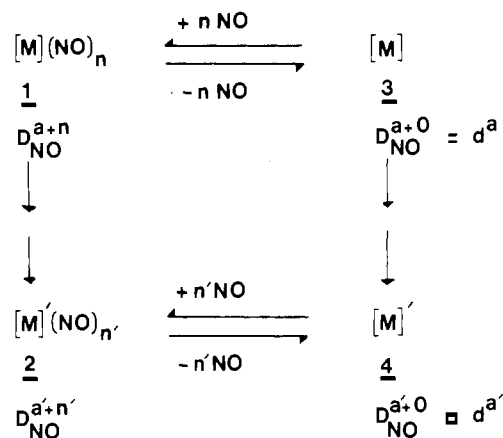
A Notation for Describing Redox Processes in the Surface Chemistry of Nitrosyl Complexes

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Received September 24, 1987

It is common to describe the reactions of nitric oxide with metallic centers on oxides or in zeolites in terms of an oxidation or a reduction of the metallic element. Unfortunately, this is not devoid of ambiguities in view of the amphoteric nature of the NO ligand.¹ For example, formation of a mononitrosyl cobalt from

Scheme I



the reaction of NO gas with a Co^{2+} -exchanged zeolite A has been interpreted either as no redox change² or as an oxidation.³ On Co^{2+} -exchanged zeolite Y, reaction with NO to yield a surface dinitrosyl has been regarded either as a reduction⁴ of the Co or as a redox-inactive process.^{2,5} On the other hand, we recently reported the formation of a similar dinitrosyl species following the deposition of $\text{Co}(\text{CO})_3\text{NO}$ on either Al_2O_3 or zeolite Y,⁷ but we described the reactions in terms of an oxidation of the cobalt sites.

We propose a shorthand notation for specifying the type of metallic centers present in NO complexes that should remove any ambiguity as to what the terms oxidation and reduction refer during reactions with nitrosylated species, whether they occur under heterogeneous or homogeneous conditions.⁸ This notation becomes equivalent to the familiar d^a notation of the formal electronic configuration of the metal in a nonnitrosylated transition-metal complex.⁹

Notation

Any $[\text{M}](\text{NO})_n$ complex can always be constructed in a formal way by the complexation of n NO molecules on the center $[\text{M}]$ where the square brackets stand for an unspecified set of non-nitrosyl ligands. If the electron configuration of the metal in the NO-free species $[\text{M}]$ is d^a , then the same metal center in the $[\text{M}](\text{NO})_n$ complex can be represented as being of type $\text{D}_{\text{NO}}^{a+n}$. In this notation, a is the number of d electrons in $[\text{M}]$ left by the dissociation (D) of the n NO ligands removed in the molecular form. In addition, according to the notation of Enemark and Feltham,¹⁰ if the complex type of $[\text{M}](\text{NO})_n$ is $\{\text{M}(\text{NO})_n\}^b$, then one has $b = a + n$ and the complex type can be rewritten as $\{\text{M}(\text{NO})_n\}^{a+n}$, as suggested previously by us,⁷ which contains the same information as the $\text{D}_{\text{NO}}^{a+n}$ notation except that the structural parameter n (the number of NO ligands) is not repeated. Note that for the NO-free species $[\text{M}]$ the metallic center becomes of

(1) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060. (b) Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26. (c) Collman, J. P.; Farnham, P.; Dolcetti, G. *J. Am. Chem. Soc.* **1971**, *93*, 1788.

(2) Lunsford, J. H.; Hutta, P. J.; Lin, M. J.; Windhorst, K. A. *Inorg. Chem.* **1978**, *17*, 606.
 (3) Cruz, W. V.; Leung, P. C. W.; Seff, K. *Inorg. Chem.* **1979**, *18*, 1692.
 (4) Praliaud, H.; Coudurier, G. F.; Ben Taarit, Y. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 3000.
 (5) Iizuka, T.; Lunsford, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 6106.
 (6) Rouston, J. L.; Lijour, Y.; Morrow, B. A. *Inorg. Chem.* **1987**, *26*, 2509.
 (7) Morrow, B. A.; Baraton, M. I.; Lijour, Y.; Rouston, J. L. *Spectrochim. Acta, Part A* **1987**, *43A*, 1583.
 (8) For reviews on the chemistry of NO complexes under homogeneous conditions, see: (a) Connelly, N. G. *Inorg. Chim. Acta, Rev.* **1972**, *6*, 47. (b) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (c) Bottomley, F. *Acc. Chem. Res.* **1978**, *11*, 158. (d) Caulton, K. G. *Coord. Chem. Rev.* **1978**, *26*, 7. (e) Reference 1b.
 (9) See, for example: Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977.
 (10) Enemark, J. E.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. A nitrosyl of type $\{\text{M}(\text{NO})_n\}^b$ contains n NO ligands and b electrons in molecular orbitals predominantly metallic d and/or π^*_{NO} in character. The parameter b could also be viewed as the number of metallic d electrons if the NO ligands were all treated formally as NO^+ , irrespective of their actual coordination mode, linear or bent.¹¹