relative ligand binding energies, (4) determination of the basicity of transition metal complexes, (5) examination of processes involving both electrophilic and nucleophilic attack on transition metal complexes, and (6) generation and study of unusual σ- and π-bonded organometallic complexes. *Such experiments are of particular interest since they provide information relating to intrinsic properties and reactivity of the species considered, in the absence of complicating solvation phenomena.*

Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3)767-8.

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Received April 5, 1971

Preparation and Structure of $Co_4(NO)_8(NO_2)_2(N_2O_2)$, A Novel Complex Containing a Quadridentate Hyponitrite Group

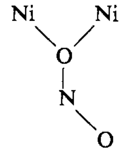
Sir:

We wish to report the synthesis and crystal structure determination of a novel complex containing the hitherto unknown linkage of a trans hyponitrite group, $(ONNO)^{2-}$, bridging four different cobalt atoms.

Synthesis. The compound $Co_4(NO)_8(NO_2)_2(N_2O_2)$ was prepared by the reaction of $Co(CO)_3NO$ and gaseous NO in a sealed, inverted J shaped tube. The sample of $Co(CO)_3NO$ was kept in the short arm of the tube, and the long arm was heated at 50–60°. The pressure of NO (which was in excess) in the tube was about 20 atm, and the tube was protected from any exposure to light. After 5–10 days of heating, two black crystalline products were formed. Needles growing at the walls of the heated portion of the tube were shown to be the recently reported polymeric dinitrosyl cobalt nitrite, $[Co(NO)_2(NO_2)]_n$.[1] The second type of crystalline product, isolated from the unheated portion of the tube and representing about 2–5% of the total product, was proved crystallographically to have the molecular formula $Co_4(NO)_8(NO_2)_2(N_2O_2)$. Unlike $Co(NO)_3$, small yields of which are also formed at 60°,[2] both of these products are insoluble in organic liquids and lack air sensitivity.

Because of the small yields of $Co_4(NO)_8(NO_2)_2(N_2O_2)$, and the difficulty of extending the preparative procedure to a larger scale, a detailed elemental analysis of the compound was not possible. However, support for the above chemical formulation was provided by an analysis of the gaseous products from the original reaction mixture, which showed that a quantitative amount of CO was evolved (0.686 mmol of CO from 0.231 mmol of $Co(CO)_3NO$). This indicated a lack of carbon in the crystalline product. The presence of NO_2 in the product was supported by the detection of N_2O in the gaseous mixture. Upon pyrolysis of $Co_4(NO)_8(NO_2)_2(N_2O_2)$, neither CO nor CO_2 could be detected, again proving the absence of carbon in the material. Less anticipated was the formation of N_2O (along with NO but not NO_2) during this pyrolysis. This N_2O, however, is believed to be a secondary product (not present as a ligand in the original complex), for no N_2O was produced by heating the compound with iodine at 100°. The absence of NO_2 during pyrolysis is not inconsistent with the behavior of other nitrite compounds, such as $[Co(NO)_2(NO_2)]_n$, which also give N_2O but no NO_2 when heated.

The infrared spectrum of $Co_4(NO)_8(NO_2)(N_2O_2)$ showed two strong NO stretches at 1850 and 1796 cm^{-1}, which are easily assignable to the terminal NO groups. Additional bands were observed at 1377 (s, close doublet), 1327 (s), 1098 (m), and 828 cm^{-1} (m). In the absence of any other reported examples of complexing hyponitrite groups[3] and the rather doubtful assignment[4] of



vibrations in $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3 \cdot C_6H_6$,[5] we believe it would be premature to assign any of the four lower frequency peaks specifically to the bridging hyponitrite *vs.* nitrite group found in our complex.

The mode of formation of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ is worthy of discussion. Gaseous NO is known to disproportionate into N_2O and NO_2, through the presumed intermediate N_2O_2.[6] It is therefore likely that, under our conditions, the system $Co(CO)_3NO + NO$, which under other conditions produces $Co(NO)_3$,[2] absorbs NO_2 to form nitrite-containing compounds. The formation of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ evidently depends not only upon the known disproportionation of gaseous NO into N_2O and NO_2[6] but also upon a reductive dimerization of NO. The conditions for the latter may be fairly critical, since the crystals were found only in the cool part of a partially heated tube. For high-yield formation of $Co(NO)_3$,[2] one works at lower temperatures and pressures, so that the alteration of the NO is minimized. It is curious that the polymeric $[Co(NO)_2(NO_2)]_n$ could be formed directly from gaseous reactants.

Structural Determination. Crystals of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ were mounted into thin-walled capillary tubes. Weissenberg and precession photographs indicated that the space group is monoclinic, $P2_1/c$, with $a = 8.26$, $b = 9.34$, $c = 12.29$ Å, and $\beta = 99.48°$. Density determinations were not feasible because the compound is affected by water and halogenated solvents.

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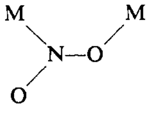
(1) C. E. Strouse and B. I. Swanson, *Chem. Commun.*, 55 (1971).

(2) I. H. Sabherwal and A. B. Burg, *ibid.*, 1001 (1970).

(3) Although the vibrational bands of the $N_2O_2{}^{2-}$ ion itself are well characterized, we feel that such assignments are of little help in assigning the vibrational bands of our compound.

(4) We feel that the assignments in ref 5 seem doubtful because of the contradictions in their assignments of the



bands with those reported in ref 1.

(5) D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha, and D. Rogers, *Chem. Commun.*, 1383 (1969).

(6) T. P. Melia, *J. Inorg. Nucl. Chem.*, 27, 95 (1965).

Two quadrants of data were collected on an automated Nonius CAD-3 diffractometer with Mo Kα radiation up to a limit of 50° in 2θ. After the results were merged, a total of 1388 reflections was found with intensities larger than 3σ. These were used in the ensuing structure analysis. The positions of the two independent cobalt atoms in the unit cell were unambiguously determined from a Patterson map. A structure factor calculation[7] based on the cobalt atom positions revealed the other atomic positions clearly, including that the of trans hyponitrite group. A succession of isotropic least-squares refinement cycles, followed by two cycles of full anisotropic least-squares refinement, led to a final R factor of 6.0%. A final difference fourier showed no residual electron density larger than 1 e/Å^3.

The geometry of this molecule is shown[8] in Figure 1. A crystallographically imposed inversion center passes through the midpoint of the N_1–N_1' bond. The various bond lengths in the molecule are given in Table I and the bond angles in Table II.

Table I. Bond Lengths (Å) in $Co_4(NO)_8(NO_2)_2(N_2O_2)$

Co_1–N_2	1.656	Co_1–O_1	1.958
Co_1–N_3	1.644	Co_1–O_6	2.009
Co_2–N_4	1.662	Co_2–N_1	1.991
Co_2–N_5	1.649	Co_2–O_6	1.976
N_2–O_2	1.151	N_1–O_1	1.316
N_3–O_3	1.137	N_1–N_1'	1.265
N_4–O_4	1.121	N_6–O_6	1.354
N_5–O_5	1.146	N_6–O_7	1.199

Table II. Bond Angles (deg) in $Co_4(NO)_8(NO_2)_2(N_2O_2)$

O_6–Co_1–O_1	86.7	Co_1–N_2–O_2	162.1
O_6–Co_1–N_3	114.8	Co_1–N_3–O_3	164.0
N_3–Co_1–N_2	108.8	Co_2–N_4–O_4	163.3
N_2–Co_1–O_1	115.0	Co_2–N_5–O_5	166.5
O_6–Co_1–N_2	114.5		
N_3–Co_1–O_1	115.9	Co_2–N_1–O_1	125.7
		Co_2–N_1–N_1'	121.8
O_6–Co_2–N_4	118.6	O_1–N_1–N_1'	112.5
O_6–Co_2–N_5	116.4	Co_1–O_1–N_1	120.9
O_6–Co_2–N_1	84.5		
N_1–Co_2–N_4	107.5	Co_1–O_6–Co_2	121.9
N_1–Co_2–N_5	112.5	Co_1–O_6–N_6	120.6
N_5–Co_2–N_4	113.3	Co_2–O_6–N_6	117.4
		O_6–N_6–O_7	112.9

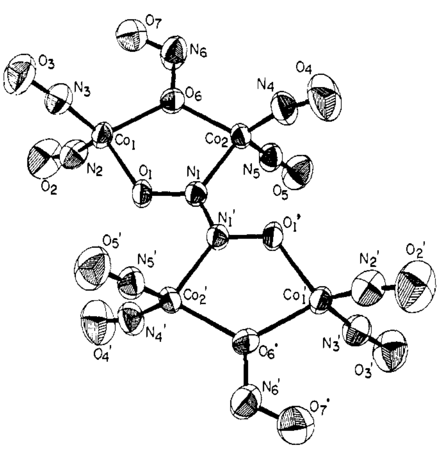


Figure 1. The geometry of $Co_4(NO)_8(NO_2)_2(N_2O_2)$.

The most remarkable feature of the molecule is clearly the trans hyponitrite group. The only other reported case of a transition metal–hyponitrite complex is the 1,3-bridging cis hyponitrite found in $\{[Co(NH_3)_5]_2(N_2O_2)\}^{4+}$, in which $Co(NH_3)_5$ moieties were attached to the 1-oxygen and 3-nitrogen atoms.[9] Crystallographic structure determinations on various nontransition metal compounds having an (ONNO) linkage have been reported; most of them contain the four-atom group in a cis configuration, as in $[(N_2O_2)SO_3]^{2-}$ [10] and $[(N_2O_2)CH_2(N_2O_2)]^{2-}$,[11] and occasionally in the trans configuration, as in $(NO_2)CH_2CH_2(ONNO)CH_2CH_2(NO_2)$.[12] The bond distances in our compound are very close to those found in $\{[Co(NH_3)_5]_2(N_2O_2)\}^{4+}$ (see Table III), but differ significantly from those in the nontransition metal hyponitrites, especially $[(N_2O_2)SO_3]^{2-}$ and $(NO_2)CH_2CH_2(N_2O_2)CH_2CH_2(NO_2)$, whose N-N bonds are about 0.05 Å longer. This probably indicates a higher N-N bond order in the transition metal hyponitrites.

Table III. Bond Distances (Å) in Various Hyponitrite Compounds

Compound	$\overset{a}{O—}$ a	$\overset{b}{N—}$ b	$\overset{c}{N—O}$ c	Ref
$Co_4(NO)_8(NO_2)_2(N_2O_2)$	1.316	1.265	1.316	This work
$[Co(NH_3)_5](N_2O_2)[Co(NH_3)_5]^{4+}$	1.29	1.25	1.32	9
$[(N_2O_2)SO_3]^{2-}$	1.286	1.327	1.284	10
$[(N_2O_2)CH_2(N_2O_2)]^{2-}$	1.266	1.297	1.323	11
$(NO_2)CH_2CH_2(N_2O_2)CH_2CH_2(NO_2)$	1.26	1.31	1.26	12

Also noteworthy is the unusual nitrite linkage previously found in only one other compound, $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3 \cdot C_6H_6$ as reported by Rogers, *et al.*[5] In that paper, attention was drawn to the stability of the five-membered ring system

$$\underbrace{M\text{-}N\text{-}O\text{-}M\text{-}O}$$

which is also present in our compound. One other remarkable feature is that the whole $Co_4(NO)_8(NO_2)_2(N_2O_2)$ molecule, with the exception of the eight terminal NO groups, is essentially planar, deviating by no more than ±0.30 Å from the plane defined by the four cobalt atoms. Such a metal–nitrogen–oxygen sheet was found also in $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3 \cdot C_6H_6$.

A third interesting feature is the Co–N–O angle of the terminal NO groups. In the present compound, the four independent Co–N–O angles all lie in the range 162–167°. In the compound[1] $[Co(NO)_2(NO_2)]_n$, whose structure was solved independently by us, the two Co–N–O angles (162 and 163°) are also in this range. The question of bond angles in metal nitrosyls has received

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(7) All the major computations in this work were performed using CRYM, an integrated set of crystallographic programs developed by R. E. Marsh and D. Duchamp at the California Institute of Technology.

(8) ORTEP, the Oak Ridge thermal ellipsoid plotting program written by C. K. Johnson.

(9) B. F. Hoskins, F. D. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Commun.*, 69 (1969).

(10) G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1467 (1951).

(11) J. H. Bryden, *Acta Crystallogr.*, **21**, 581 (1959).

(12) F. P. Boer and J. W. Turley, *J. Amer. Chem. Soc.*, **89**, 1034 (1967).

considerable attention recently,[13–16] but most of the discussion has centered around angles of 180° *vs.* 120°. There is mounting evidence[17–20] that angles in the 160° range are quite prevalent in metal nitrosyls. Intermediate angles such as these are obviously not easily rationalized; it may be that better overlap between the metal and ligand orbitals can be achieved through moderate bending.

Acknowledgments. We are grateful to the National Science Foundation (Grant No. GP-17472), the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2059-G3), and the Research Corporation for supporting this research. We would also like to thank the Computer Center of the University of Southern California for making available its IBM 360/65 computer for this work.

[13] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

[14] C. G. Pierpont, D. G. Van der Veer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

[15] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

[16] D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971).

[17] D. M. P. Mingos and J. A. Ibers, *ibid.*, **9**, 1105 (1970).

[18] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, **11**, 599 (1958).

[19] G. R. Davies, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 81 (1968).

[20] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1095 (1966).

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On the Action of Europium Shift Reagents

Sir:

Since the discovery by Hinckley[1] of the large shifts in nuclear magnetic resonances produced by interaction with compounds of trivalent europium, many studies which exploit the effect for determination of structure have been carried out. This communication is intended to remind people of the analysis carried out by Van Vleck[2] about 40 years ago of the paramagnetisms of Eu,$^{3+}$ and to emphasize its bearing on interpretation of the phenomena observed with the shift reagents.

At room temperature Eu^{3+} is found in its lowest electronic state, $^7F_0$, and its first excited state at 200 cm^{-1}, $^7F_1$, with approximately equal occupation probabilities. The lowest state, $^7F_0$, is nondegenerate and has no Zeeman splitting. Hence the interactions usually cited—contact and pseudocontact—cannot operate in the lowest state. In the excited state $^7F_1$, where the crystal-field splittings are much smaller than kT, the pseudocontact and contact interactions may contribute to the shifts. The dominant contribution from the $^7F_0$ ground state is undoubtedly related to the second-order paramagnetism.

The static susceptibility of Eu^{3+} should be almost independent of temperature below $\sim$100°K. At these temperatures, a shift independent of temperature is expected. It should have the $\langle r^{-3}\rangle$ dependence on distance exhibited by the pseudocontact shift. I would expect that, because of the very small crystal-field splittings of the excited state whose admixture produces the second-order paramagnetism, the temperature-independent part of the shift would be almost isotropic.

It is unfortunate that only meager data concerning the magnetic properties of the various rare earth ions in the compounds used as shift reagents are available. Their acquisition will probably enhance the usefulness of the method.

Acknowledgment. This work has been supported by the National Science Foundation and by the Petroleum Research Fund of the American Chemical Society.

[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[2] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter IX.

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A Simple Protecting Group Protection–Purification "Handle" for Polynucleotide Synthesis. I

Sir:

In recent years chemical reactions have been carried out on polymer supports by a number of investigators with the objective of simplifying the procedures for the stepwise synthesis of complex substances such as polypeptides and polynucleotides. This method has proved a great success in the field of peptide synthesis.[1] More recently, the application of this procedure to oligonucleotide synthesis has been investigated in a number of laboratories.[2–7] However, desired sequences obtained through the present method of solid-phase synthesis are accompanied with several truncated sequences.[8]

Since it is evident that the formation of truncated sequences cannot be avoided in solid-phase synthesis, we hope to prepare desired sequences exclusively by taking advantage of separation on a solid phase, thereby overcoming the limitation of the solid-phase synthesis.

This report describes a new method of preparing oligothymidylate derivatives which may be applied to the preparation of other pure oligothymidylate sequences. The coupling reactions of nucleotides in this method were carried out in solution in the absence of polymer. In the next stage, the desired oligonucleotide was separated from the other by-products using an ion exchange resin employing salt formation or molecular adsorption between the protecting group and the ion exchange resin. A basic *N,N*-dimethyl-*p*-phenylenediamino group was chosen as a protecting group on the nucleoside 5′-phosphate end. This group was intro-

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[1] R. B. Merrifield, *Advan. Enzymol.*, **32**, 221 (1969), and references cited therein.

[2] R. L. Letsinger and V. Mahadevan, *J. Amer. Chem. Soc.*, **87**, 3526 (1965); **88**, 5319 (1966).

[3] F. Cramer, R. Helbig, H. Hettler, K. H. Scheit, and H. Seliger, *Angew. Chem.*, **78**, 640 (1966); F. Cramer and H. Köster, *ibid.*, **80**, 488 (1968).

[4] H. Hayatsu and H. G. Khorana, *J. Amer. Chem. Soc.*, **88**, 3182 (1966); **89**, 3880 (1967).

[5] L. R. Melby and D. R. Strobach, *ibid.*, **89**, 450 (1967); *J. Org. Chem.*, **34**, 421, 427 (1969).

[6] G. M. Blackburn, M. J. Brown, and M. R. Harris, *J. Chem. Soc. C*, 2483 (1967).

[7] T. Kusama and H. Hayatsu, *Chem. Pharm. Bull.*, **18**, 319 (1970).

[8] E. Bayer, H. Eckstein, K. Hägele, W. A. König, W. Brüning, H. Hagenmaier, and W. Parr, *J. Amer. Chem. Soc.*, **92**, 1735 (1970).