TABLE VIII
CALCULATION OF $E°$ FOR $V(bipy)_3^{2+,3+}$
USING THE MARCUS THEORY[a]

Oxidant	k_{12}, M^{-1} sec^{-1}	k_{22}	$E_{22}°$	$E_{11}°$
$Ru(NH_3)_6^{3+}$	0.12	$\sim 1 \times 10^{3}$ [b]	-0.10[b]	-0.81
$Co(bipy)_3^{3+}$	6.4	~ 20[c]	0.37[e]	-0.75
$Fe(EDTA)^-$	23	$>10^4$ $(>10^3$ at 0°) [d]	-0.12[f]	<-0.62
$Co(EDTA)^-$	0.054	4×10^{-7} [d]	-0.60[g]	-0.78

[a] Subscripts 1 and 2 refer to the reducing and oxidizing couples, respectively. [b] See ref 41. [c] P. Ellis, R. G. Wilkins, and R. P. J. Williams, *J. Chem. Soc.*, 4456 (1957). [d] See ref 12. [e] E. Paglia and C. Seroni, *Gazz. Chim. Ital.*, **87,** 1125 (1957). [f] G. Schwarzenbach and H. Heller, *Helv. Chim. Acta*, **34,** 576 (1951). [g] D. A. Buckingham and A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 245.

might be shifted to a more negative value by as much as 1 V when H_2O as ligand is replaced by bipy. It is likely that although there undoubtedly is a marked shift to more negative values, the shift is not quite as large as this. The replacement of H_2O on $Ru^{2+,3+}$ by bipy or phen shifts the potential by *ca.* 1 V[43,44] and the shift is expected to be greater for Ru than for V because six rather than three t_{2g} electrons are involved in back-bonding. A value of $E°$ for $V(trpy)_2^{2+,3+}$ as low as -0.8 V would moreover require k_{-1} to exceed diffusion control (10^{12} greater than $k_{-1} \cong 2$). Thus, to the extent that the Marcus theory is valid, $E°$ for $V(bipy)_3^{2+,3+}$ is indicated as being somewhat less negative than -0.8 V and k_{11} as being somewhat less than 10^7 M^{-1} sec^{-1}. A lower self-exchange rate in the t_{2g}^3–t_{2g}^2 as compared to the t_{2g}^6–t_{2g}^5 system could conceivably arise from decreased electron delocalization over the π^* ligand orbitals in the former due to decreased electron-electron repulsions.

It should be noted also that if $E°$ is as negative as -0.8 V, dissociation of bipy from $V(bipy)_3^{3+}$ must take place with a specific rate of $\sim 10^8$ sec^{-1} if inhibition by $Ru(NH_3)_6^{2+}$ is not to be observed in the $V(bipy)_3^{2+}$–$Ru(NH_3)_6^{3+}$ reaction. Though the requirement on this rate is less stringent than this if, as seems indicated, the actual value of $E_{11}°$ is less negative than -0.8 V, it yet remains clear that $V(bipy)_3^{3+}$ is very substitution labile, much more so than is $V(bipy)_3^{2+}$, the factor likely being much in excess of 10^5. With H_2O as ligands, V(III) is only slightly more labile than is V(II).[45] The change in relative lability as H_2O is replaced by bipy is probably a result of the greater advantage which the ion in the lower oxidation state can take of the capability of the conjugated ligand to interact with the t_{2g} electrons of the metal ion. The possibility is also open that when an electron is removed from $V(bipy)_3^{2+}$, a water molecule can move into the first coordination sphere of V(III) (electronic configuration t_{2g}^2). Proton dissociation from such a water molecule would take place readily, and this would facilitate release of other ligands.

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[43] See footnote *g* of Table VIII.

[44] E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4,** 1692 (1965).

[45] R. G. Wilkins and M. Eigen, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

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Novel Metal Complexes Involving a Multiply Bridged Nitrogen Atom

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A reaction of $(t\text{-}C_4H_9N)_2S$ with $(\pi\text{-}C_5H_5)_2Ni$ or $[\pi\text{-}C_5H_5Ni(CO)]_2$ produced a black, paramagnetic (1.68 BM, $g = 2.035$), trinuclear complex, $t\text{-}C_4H_9N(\pi\text{-}C_5H_5Ni)_3$ (I). The chemical and physical properties of I suggested a trigonal-pyramidal structure with an apical nitrogen atom on a triangle of nickel atoms. The preliminary results of a three-dimensional, single-crystal X-ray analysis confirmed this structure and revealed a considerable distortion from C_{3v} symmetry. The three Ni–Ni distances are 2.34, 2.27, and 2.21 Å. A similar reaction of $(t\text{-}C_4H_9N)_2S$ with $\pi\text{-}C_5H_5Co(CO)_2$ gave a dark green, binuclear diamagnetic complex, $(\pi\text{-}C_5H_5Co)_2(t\text{-}C_4H_9N)_2CO$ (II). Based on the physical measurements, the structure of II was deduced to be a di-*t*-butylurea complex where each nitrogen atom bridges the two cobalt atoms. The crystal structure has also been determined from single-crystal X-ray analysis which revealed a short Co–Co distance (2.367 Å). A reaction scheme involving a metal–nitrene intermediate was proposed for the formation of II.

Introduction

Recently, there have been found a number of polynuclear organometallic complexes which involve metal–metal bonds. They are subjects of growing interest regarding their chemical structure as well as the physical properties such as temperature-dependent magnetic behavior.[1] Studies on the reaction of N-*t*-butylsulfurdiimide, $(t\text{-}C_4H_9N)_2S$, with bis(π-cyclopenta-

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[1] J. Lewis, "Plenary Lecture at VIIIth International Conference on Coordination Chemistry, Vienna, Austria, 1964," Butterworth and Co. Ltd., London.

dienyl)nickel or π-cyclopentadienylnickel carbonyl, $[\pi\text{-}C_5H_5Ni(CO)]_2$, and with π-cyclopentadienylcobalt dicarbonyl led us to find new polynuclear complexes involving metal–metal bonds and a nitrogen or sulfur atom multiply bridged between the metal atoms. Facile cleavage of the N–S bond of $(t\text{-}C_4H_9N)_2S$ enables us to obtain these complexes in fairly good yield. Synthetic and structural chemistries of the two nitrogen complexes, one containing nickel atoms and the other cobalt atoms, are described below.

Experimental Section

N-*t*-Butylsulfurdiimide was prepared according to the method of Clemens, *et al.*[2] The preparative work and physical measurements which involve organometallics were carried out under nitrogen.

Preparation of $t\text{-}C_4H_9N(NiC_5H_5)_3$ (I).—A mixture of 1.14 g (6 mmol) of $(\pi\text{-}C_5H_5)_2Ni$ and 0.54 g (3 mmol) of $(t\text{-}C_4H_9N)_2S$ in 30 ml of heptane was refluxed for 7 hr. The filtered solution was concentrated under vacuum and chromatographed on deoxygenated alumina using a benzene–heptane (1:1) mixture as an eluent to give 0.55 g (62% yield) of black cubic crystals as a main product. Recrystallization from a benzene–heptane mixture and sublimation at 150° (2.7×10^{-3} mm) gave an analytical sample of a nitrogen-containing complex (I), dec pt *ca.* 180°.

Anal. Calcd for $C_{19}H_{24}NNi_3$: C, 51.55; H, 5.46; N, 3.16; mol wt, 440. Found: C, 51.74, 51.65; H, 5.77, 5.46; N, 2.91; mol wt, 440 (mass spectrometry).

Alternatively, a mixture of 0.3 g (1 mmol) of $[\pi\text{-}C_5H_5Ni(CO)]_2$ and 0.36 g (2 mmol) of $(t\text{-}C_4H_9N)_2S$ in 10 ml of heptane was refluxed for 2 hr and the reaction mixture was worked up similarly to give 30 mg (10% yield) of the same black cubic crystals.

Acid Hydrolysis of I.—To a solution of 187 mg (0.425 mmol) of I in 20 ml of ethanol was added 5 ml of 5 *N* HCl and the mixture was heated at 60° for 1 hr. After filtration, the filtrate was concentrated to give a residue which was then dissolved in dilute aqueous sodium hydroxide and treated with 300 mg (2.1 mmol) of benzoyl chloride to give a crude acylated product. The product was taken up in diethyl ether and washed with dilute alkali, dried, and evaporated to give 30 mg (40% yield) of colorless needles, mp 135–135.5°, which was identified, based on its mixture melting point test and infrared spectrum, to be $C_6H_5CONH(t\text{-}C_4H_9)$.

Some Electron-Transfer Reactions. a. Reduction of I with Metallic Potassium.—The reaction was carried out under nitrogen in a vacuum system consisting of a sealed tube connected with an nmr sample tube through a glass filter and a tube for preparation of the sample solution. To the freshly prepared metallic potassium film (*ca.* 0.3 g) was added 0.1 g (0.23 mmol) of I dissolved in 2 ml of oxygen-free dry tetrahydrofuran. The mixture was allowed to stand at room temperature for 2 days, to give a dark brown slurry. The nmr spectrum of the filtrate obtained from the slurry was measured using tetrahydrofuran as an internal standard; it showed two singlets at τ 2.62 and 8.86, which were ascribable to the cyclopentadienyl anion protons and the methyl protons of the *t*-butyl group.

b. Oxidation of I with Cupric Acetate.—To a dilute solution of I in tetrahydrofuran (dark brown) was added a cupric acetate solution of tetrahydrofuran at ambient temperature. Immediate discoloration of the dark brown solution to pale yellow took place without any precipitation. Free cyclopentadiene was detected by gas chromatography of the reaction mixture indicating complete destruction of I. An indication for reduction of the cupric ion to a cuprous ion was obtained spectroscopically.

Physical Measurements of I.—The infrared spectrum was measured with a Jasco Model DS-402G grating spectrophotometer using a Nujol mull. The spectrum shows a skeletal vibration frequency of the *t*-butyl group at 1195 cm^{-1} and the characteristic bands ascribable to the π-bonded cyclopentadienyl group at 3060, 1420, 1110, 1004 (sh), 1002, 802, 781, and 355 cm^{-1}. Besides these, there are unassignable bands at 675 (s), 600 (w), 408 (w), and 265–280 cm^{-1} (w).

The electronic spectrum was recorded with a Hitachi recording spectrophotometer, Model EPS-2, using tetrahydrofuran solution. The absorption maxima (mμ) occurred at 378 (ϵ 1.50×10^4), 560 (ϵ 1.25×10^3), and 720 (ϵ 9.8×10^2).

The magnetic susceptibility χ_{mole} measured by a Gouy balance was 3750×10^{-6} and 384×10^{-6} cm^3/mole at 77 and 393°K, respectively, corresponding to a magnetic moment of 1.68 BM.

The esr spectrum was recorded at room temperature with a Tokyo Denki Model 5000 epr spectrophotometer of 100-kc field modulation X band. The benzene solution or a polycrystalline sample of I showed a singlet with a line width of 29 gauss without hyperfine structures. The *g* value was 2.035.

Owing to the paramagnetism, I shows no identifiable nmr absorption.

Mass Spectroscopic Analysis of I.—The mass spectrum was measured with a Hitachi Type RMU-7HR. Three peaks of *m/e* 440 (relative intensity 100), 425 (33), and 383 (43) appear to be key bands corresponding to fragment ions $C_4H_9N(NiC_5H_5)_3^+$, $C_3H_6N(NiC_5H_5)_3^+$, and $N(NiC_5H_5)_3^+$, respectively. The relative intensities for series of isotope peaks to be seen with respect to the key peak of, *e.g.*, *m/e* 440 were calculated by adding the nickel and carbon isotope corrections (Table I). An expansion of $(a + b + c + d)^n$, where a, b, c, and d are relative abundances of Ni^{58}, Ni^{60}, Ni^{61}, and Ni^{62}, respectively, and n is the number of nickel atoms involved (in this example $n = 3$), was used to obtain the relative intensities for $m + 1$, $m + 2$, $m + 3$, $m + 4$, and $m + 5$, due to nickel isotopes. Table I shows fairly good agreement between the observed and the calculated relative intensities for *m/e* 440 ions. The key peak at *m/e* 425 also showed isotope peaks whose relative intensities were in good agreement with the calculated ones. Thus the mass spectrum of I has revealed a three-nickel atom cluster ion bridged by a tertiary nitrogen atom, each nickel atom carrying a cyclopentadienyl group.

TABLE I

RELATIVE INTENSITIES OF THE $t\text{-}C_4H_9N(NiC_5H_5)_3^+$ ION

	Relative intensity					
	m (440)	$m + 1$ (441)	$m + 2$ (442)	$m + 3$ (443)	$m + 4$ (444)	$m + 5$ (445)
Found	100	24	118	31	63	15
Calcd	101	20	118	30	63	15
Based on Ni	101	0	118	5	62	3
Based on C^{13}	0	20	0	25	1	12

Preparation of $(C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$ (II).—A mixture of 2.4 g (13.3 mmol) of $C_5H_5Co(CO)_2$ and 2.4 g (13.8 mmol) of $(t\text{-}C_4H_9N)_2S$ in 30 ml of heptane was refluxed for 5 hr to give a dark-colored slurry whose solid part (black) contained sulfur compounds. The solid was filtered off after cooling. The filtrate was concentrated under vacuum and chromatographed on deoxygenated alumina under nitrogen using a benzene–*n*-hexane (1:1) mixture to give a dark green solution of a nitrogen-containing complex. The crude complex obtained from the concentrated eluate was contaminated with a small amount of an organic compound. Fractional sublimation at 100° (3 mm) separated 58 mg (2.1% yield) of the dark green complex free from the colorless organic compound which was identified as di-*t*-butylurea, $[(CH_3)_3CNH]_2CO$, based on its infrared spectrum.

Anal. Calcd for $C_{19}H_{28}N_2OCo$: C, 54.75; H, 6.70; N, 6.70; mol wt, 418. Found: C, 54.35; H, 6.75; N, 6.59; mol wt, 418 (mass spectrometry) and 412 (vapor pressure osmometry using benzene as a solvent).

The insoluble part precipitated from the cooled reaction mixture contains sulfur but no nitrogen atom. Alumina chromatography of this black solid gave two sulfur-containing polynuclear complexes, $(C_5H_5Co)_3S_2$ and $(C_5H_5Co)_3(CO)S$, together

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[2] D. H. Clemens, A. J. Bell, and J. L. O'Brien, *Tetrahedron Letters*, 1487 (1965).

with di-*t*-butylurea. The isolation and structural studies of these sulfur complexes will be given elsewhere.[3]

Physical Measurements of II. The infrared spectrum measured by using a Nujol mull shows ν_{CO} frequency at 1695 and 1672 cm^{-1}, $\delta_{C(CH_3)_3}$ frequency at 1217 cm^{-1}, and the characteristic bands due to the π-bonded cyclopentadienyl group at 3080, 1409, 1106, 1002, 994, 808, 795, and 370 cm^{-1}. Unassignable bands appeared at 692, 585, 485, 425, 323, 240, and 220 cm^{-1}. The sample dissolved in CCl_4 showed a strong carbonyl band at 1684 cm^{-1} with a slight shoulder at about 1675 cm^{-1}.

The nmr spectrum was measured with a 100-Mc Japan Electron Optics Laboratory Model JNM 4H-100 in benzene solution using TMS as an internal reference. The spectrum showed two singlet resonances at τ 5.31 and 8.49 with a relative intensity of 5:9.5 which were assigned to the five π-bonded cyclopentadienyl protons and the nine methyl protons of the *t*-butyl group, respectively.

Table II shows a part of the mass spectrum of II.

TABLE II

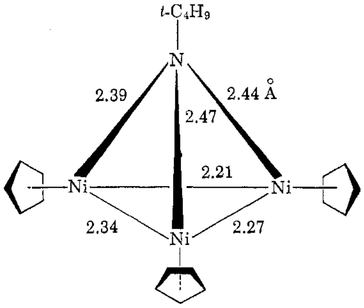
MASS SPECTRUM OF $(\pi\text{-}C_5H_5Co)_2(NC_4H_9)_2CO$

m/e	Rel intens	Assignment	*m/e*	Rel intens	Assignment
418	5	$(C_5H_5Co)_2(C_4H_9N)_2CO^+$	248	36	$(C_5H_5Co)_2{}^+$
361	7	$(C_5H_5Co)_2\ C_4H_9N)CON^+$	203	100	$(C_5H_5)_2CoN^+$
346	10	$(C_5H_5Co)_2(C_3H_6N)CON^+$	189	260	$(C_5H_5)_2Co^+$
318	14	$(C_5H_5Co)_2(C_3H_6N)N^+$	180	48	$C_5H_5CoC_3H_6N^+$
304	6	$(C_5H_5Co)_2CON^+$ or	165	96	$C_5H_5CoC_2H_3N^+$
		$(C_5H_5Co)_2C_3H_6N^+$	144	14	Co_2NC^+
288	2	$(C_5H_5Co)_2CN_2{}^+$	143	20	$C_4H_9NNHC_4H_9{}^+$
274	4	$(C_5H_5Co)_2CN^+$	125	42	$C_4H_9N(CO)NC^+$
262	10	$(C_5H_5Co)_2N^+$	97	17	$C_4H_9NCN^+$
260	16	$(C_5H_5Co)_2C^+$			

Attempted Reactions of $(t\text{-}C_4H_9N)_2S$ with Some Second-Row Metal Complexes.—The reactions of $(t\text{-}C_4H_9N)_2S$ with several second-row transition metal compounds such as $Rh[P(C_6H_5)_3]_3Cl$, $[Rh(CO)_2Cl]_2$, and $Pd[P(C_6H_5)_3]_4$ in benzene resulted in merely recovery of the starting materials.

The Structural Chemistry

The Nickel Complex (I).—A dark-colored complex (I) containing a nitrogen atom was a main product in the reaction of N-*t*-butylsulfurdiimide with bis(π-cyclopentadienyl)nickel or π-cyclopentadienylnickel carbonyl; no identifiable sulfur complex was detected. Complex I sublimes under vacuum without appreciable decomposition when the bath temperature is kept below 150°. It is not extremely air sensitive, but deteriorates slowly in air. The molecular formula $C_4H_9N(NiC_5H_5)_3$ was immediately evident from the molecular weight measurement and elemental analysis. The infrared spectrum indicated the presence of the *t*-butyl group and of the π-cyclopentadienyl ring. Acid hydrolysis of I in aqueous alcohol readily took place yielding *t*-butylamine detected as its benzoyl derivative; the facile protolysis suggests that the $(CH_3)_3CN\!<$ group may be triply bonded to three nickel atoms. Based on these data, the skeleton of I may be constructed as a trigonal pyramid with an apical nitrogen atom on the basal nickel triangle with a reservation regarding involvement of metal–metal bonding. The mass spectrum offered a strong support for the postulated structure involving a nickel cluster. A parent peak of *m/e* 440 corresponding to $C_4H_9N(NiC_5H_5)_3{}^+$ appeared with a number of isotope peaks. The calculated relative intensities for these isotope peaks of *m/e* 441, 442, 443, etc., agree well with the observed relative intensities as shown in Table I. Similar agreement was observed for a peak of *m/e* 425 which corresponds to $C_3H_6N(NiC_5H_5)_3{}^+$. A peak of *m/e* 383 then appears to be due to a fragment ion $N(NiC_5H_5)_3{}^+$ produced by cleavage of the *t*-butyl group from the parent ion *m/e* 440. In the mass spectrum of a metal cluster complex one can observe the cluster ion which preserves the original configuration of the cluster, *e.g.*, $YCCo_3{}^+$ [4] and $Co_4{}^+$ [4] from $YCCo_3(CO)_9$ and $Co_4(CO)_{12}$, respectively. Thus the peaks at *m/e* 383 as well as at 425 may imply a three-nickel cluster. The structure A is now proposed for complex I. This was confirmed by a three-dimensional, single-crystal X-ray diffraction.[5] The X-ray examination shows that the monoclinic unit cell contains eight units of I with $a = {\sim}28.4$, $b = {\sim}9.16$, $c = {\sim}15.28$ Å, $\beta = 100°\ 30'$, and space group C2/C. Although an exact determination by refinement for the atomic parameters has not been concluded yet, calculation of the three-dimensional Patterson and Fourier syntheses allows us to deduce roughly the molecular structure as a trigonal pyramid with a basal scalene triangle of nickel atoms and an apical nitrogen atom situated at a distance of ~1.87 Å above the plane. The preliminary interatomic distances are given in Figure 1.[5a] The X-ray analysis clearly indicates a considerable distortion from C_{3v} symmetry. This finding, at first sight rather unexpected, is in contrast to the reported D_{3h} symmetry[6] for the closely related complex tris(cyclopentadienylnickel) dicarbonyl, $(C_5H_5Ni)_3(CO)_2$,[7] which is paramagnetic (1.79 BM).



A

Figure 1.—The molecular structure of $t\text{-}C_4H_9N(\pi\text{-}C_5H_5Ni)_3$.

The paramagnetism (1.68 BM) of I and its esr spectrum indicated the presence of one unpaired electron somewhere save in the neighbor of the quaternary nitrogen atom. Identification of the orbital of the odd electron may be accomplished by more detailed spectroscopic information such as anisotropic *g* values, with the help of extended theory of *g* values to cover the

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[3] S. Otsuka, A. Nakamura, and T. Yoshida, to be published.

[4] R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

[5] N. Kamijo, *et al.*, to be published.

[5a] NOTE ADDED IN PROOF.—The three internickel and three nitrogen–nickel distances (Å) from the latest X-ray data are: Ni^1–Ni^2, 2.39; Ni^2–Ni^3, 2.37; Ni^3–Ni^1, 2.34; N–Ni^1, 1.60; N–Ni^2, 1.80; N–Ni^3, 1.73; $R = 0.17$.

[6] H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, **5**, 417 (1962).

[7] E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958).

case in which several nuclei contribute to the spin-orbit coupling energy. Tentatively, we assume that the unpaired electron is in a π-orbital consisting essentially of 3d nickel orbitals. Based on this assumption, the observed distortion including a short internickel distance (~2.2 Å) may be explicable in terms of the Jahn-Teller theorem. The deformation may as well be caused to some extent by a crystal field in the lattice.

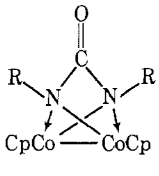
The established structure A (see Figure 1) offers general interest in several respects; *viz.*, (1) it may be regarded as a first reported example of a *metal-stabilized nitrene* or *nitrenoid* complex, (2) the classical valence bond theory calls for a positive charge on the quadruply σ-bonded nitrogen introducing an intramolecular charge separation, and (3) it is a new three-metal cluster containing an unpaired electron of relatively low ionization potential whose location presents a challenging problem as mentioned above. The last point may need comment. A brief study on a reaction of I with cupric acetate in tetrahydrofuran revealed that a facile electron transfer resulted in the destruction of the complex. An attempted introduction of an electron into I by potassium metal in tetrahydrofuran at ambient temperature led to a mixture including cyclopentadienide anion and a *t*-butylamine derivative unidentifiable owing to its extreme air sensitivity.

The Cobalt Complex (II).—A reaction of di-*t*-butylsulfurdiimide with π-cyclopentadienylcobalt dicarbonyl in heptane produced a dark green, diamagnetic complex (II) in small yield and two dark, almost black sulfide complexes, $(\pi\text{-}C_5H_5Co)_3S_2$ (III) and $(\pi\text{-}C_5H_5Co)_3(CO)S$ (IV). Besides these complexes di-*t*-butylurea was detected in the reaction products. Structural assignments of III and IV will be described elsewhere.

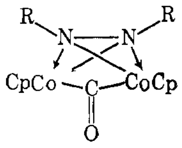
$$(t\text{-}C_4H_9N)_2S + \pi\text{-}C_5H_5Co(CO)_2 \longrightarrow \begin{cases} (\pi\text{-}C_5H_5Co)_2(t\text{-}C_4H_9N)_2CO \text{ (II)} \\ (\pi\text{-}C_5H_5Co)_3S_2 \text{ (III)} \\ (\pi\text{-}C_5H_5Co)_3(CO)S \text{ (IV)} \\ (t\text{-}C_4H_9NH)_2CO \end{cases}$$

Complex II, quite stable in air, can be sublimed under atmospheric pressure near its melting point (165–168°) without appreciable decomposition. It dissolves readily in most organic solvents such as *n*-hexane, ethers, and alcohols, the solubility being greater in polar solvents like alcohols than in nonpolar ones. A molecular formula $(C_5H_5Co)_2(NC_4H_9)_2CO$ was found from the elemental analysis and molecular weight measurement carried out by cryoscopic and mass spectrometric means. The infrared spectrum indicates the presence of π-cyclopentadienyl, *t*-butyl, and carbonyl groups. The Nujol-mulled sample shows two carbonyl stretchings at 1695 and 1672 cm^{-1}, whereas the solution sample in carbon tetrachloride exhibits one strong band at 1684 cm^{-1} with a slight shoulder around 1675 cm^{-1}. These frequencies are somewhat lower than those commonly found for the bridging metal carbonyl group and within the range of alkylurea carbonyl stretchings (~1660 cm^{-1}).[8] The nmr spectrum shows two singlets at τ 5.31 and 8.49, with a relative intensity of 5:9.5, which are assignable to the π-cyclopentadienyl and methyl protons of *t*-butyl groups, respectively. That only one singlet absorption is observable in the higher field indicates that the two *t*-butyl groups are equivalent. Also the two π-cyclopentadienyl rings should be equivalent.

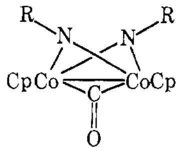
The mass spectrum of II (Table II) shows the parent ion, $(C_5H_5Co)_2(t\text{-}C_4H_9N)_2CO^+$, and a number of binuclear ions such as $(C_5H_5Co)_2(RN)CON^+$, $(C_5H_5Co)_2N^+$, $(C_5H_5Co)_2C^+$, and $(C_5H_5Co)_2^+$. The strongest peak is the stable cation $(C_5H_5)_2Co^+$. There are a considerable number of peaks, *e.g.*, *m/e* 346, 304, 288, and 125, which point to the presence of an N–CO–N group. Despite the peaks at *m/e* 318 and 143,[9] the over-all fragmentation pattern clearly indicates reluctance to release the carbonyl group; this could not be the case for a metal carbonyl group.[4,10] Thus the mass and infrared spectra consistently suggest that the organic moiety in II is an alkylurea whose nitrogen atoms bridge the two cobalt atoms. All of these physical measurements mentioned above served to corroborate the structural assignments to be B rather than a metal carbonyl complex such as C or D.



B



C



D

This was finally verified by a three-dimensional, single-crystal X-ray diffraction.[11] To avoid repetition only the major feature of the result is given in Figure 2.

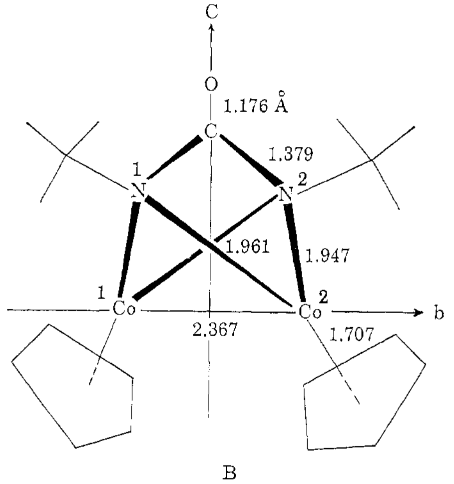


Figure 2.—The molecular structure of $(\pi\text{-}C_5H_5Co)_2(t\text{-}C_4H_9N)_2CO$. Angles: $N^1Co^1N^2$, 66.4°; $N^1Co^1Co^2$, 52°; $Co^1N^1Co^2$, 74.6°.

The cobalt–cobalt distance, 2.367 Å, appears to be rather unexpectedly short; it is shorter than that in

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[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 223.

[9] By virtue of the X-ray structural determination we can conclude that these peaks are due to recombination of fragment ions.

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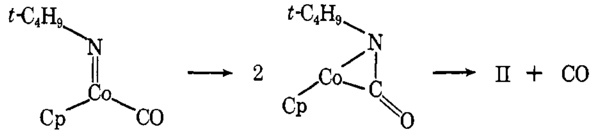
any known polynuclear cobalt complexes.[1,12,13] The two nitrogen atoms of II are quadruply σ bonded as in I whose internickel distances (2.21–2.34 Å) are the shortest so far that we are aware of. The significantly different metal–nitrogen distances in compounds I and II appear to be due to a change in the organic moiety attached to the nitrogen atom.

Complex II may be regarded as an intermediate of the formation of N,N′-di-*t*-butylurea found in the sulfurdiimide reaction. A reasonable explanation for the formation of II may be found if one assumes an insertion reaction of a carbonyl ligand into the cobalt–nitrene bonding producing an unstable isocyanate complex.



A reaction bearing on this mechanism appears to be the interaction of phenylisocyanate with triiron dodecacarbonyl which was reported to give a presumably isostructural complex, $[(C_6H_5N)_2CO]Fe_2(CO)_6$.[14]

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Transition Metal N,N-Diethyldiselenocarbamates

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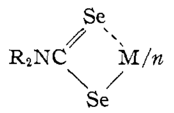
Transition metal complexes of dsc (N,N-diethyldiselenocarbamate) have been prepared with Cr(III), Co(III), Ni(II), and Pd(II), and their electronic spectra, together with those of the already known Cu(II) and Zn(II) complexes, have been investigated and interpreted in terms of a ligand field model. The spectrochemical and nephelauxetic position and the optical electronegativity value of the dsc ligand are discussed and compared with those of the analogous sulfur-containing ligand dtc.

Introduction

Among the heavy donor atoms, selenium is one of the least widely investigated. There has been some recent interest in Se-containing complexes, *e.g.*, of diselenophosphates,[1] of diselenetene and diselenato complexes,[2] of alkyl or aryl selenides,[3–5] of selenides in ZnSe or CdSe lattices,[6,7] and of selenoureas,[8–10] but as a whole our knowledge of selenium as donor atom in metal complexes is far less detailed than that of the homologous element sulfur. As a part of a research program on complexes with soft donor atoms we have studied the interesting ligand, N,N-diethyldiselenocarbamate ($(C_2H_5)_2NCSe_2^-$ = dsc), first prepared by Barnard and Woodbridge.[11] In particular we have prepared some new transition metal complexes besides the zinc and copper compounds already described by Barnard and Woodbridge[11] and have investigated particularly their spectrochemical properties.

The chemistry of complex diethyldiselenocarbamates is, as we can judge from our results, completely analogous to that of the dialkyldithiocarbamate complexes. Thus the free ligand (sodium or potassium salts, prepared from carbon diselenide and diethylamine in basic medium) reacts readily with several transition metal salts or complexes, giving monomeric, nonelectrolytic inner complexes, which are generally of the low-spin type and highly colored, much like the corresponding dialkyldithiocarbamato complexes, and contain four-membered chelate rings



We prepared and investigated the diethyldiselenocarbamates of Cr(III), Co(III), Ni(II), and Pd(II), in addition to the already known Cu(II) and Zn(II) complexes. All of these complexes are remarkably stable for selenium-containing compounds; only the Cr(III) compound undergoes decomposition more easily. The electronic spectra of such complexes resemble closely those of the corresponding dithiocarbamates, except for a general red shift of all transitions. The similarity between the chemical behavior of the

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