J. Am. Chem. Soc. 1984, 106, 6987–6993

for the iron catechol (1:1) complex over this pH range. The corrected value of 10^9, in contrast to the earlier figure of 10^{20},[25,30] is compatible with ligand competition studies.[16] It appears likely that protonation of the iron catechol complex is a prerequisite for an internal redox reaction.

Hider, Silver, and co-workers, using Mössbauer spectroscopy, demonstrated that in methanolic solutions iron(III) enterobactin undergoes an internal redox reaction under acid conditions leading to the generation of iron(II) [$\Delta E_Q = 3.41$ (2) mm s^{-1}, $\delta = 1.37$ (1) mm s^{-1}.][14] Pecoraro et al.[19] have confirmed these observations for iron enterobactin in acidic methanol ($\Delta E_Q = 3.44$ mm s^{-1}, $\delta = 1.38$ mm s^{-1}).[31]

Comparison of the Two Proposed Acid-Dependent Mechanisms for Iron Release from Catecholato Siderophores. Mechanism C (Scheme I). Raymond and co-workers have shown that in order for iron to dissociate from hexadentate siderophores in aqueous media, the complex must be triprotonated.[19] These triprotonated species begin to form at pH 5.0, and for $[\mathrm{Fe(H_3MECAMS)}]^{3-}$ 50% formation occurs at pH 3.3. Iron enterobactin and iron MECAM are both insoluble at this pH. Bacteria, unlike eukaryotes, possess a single intracellular compartment, and it is extremely unlikely that a bacterium would permit the pH of its cytoplasm to fall to these acidic pH values and thereby expose all intracellular enzymes to such acidity. Even in eukaryotic tissue, where acid intracellular compartments allow the removal of iron from transferrin, the pH barely falls below pH 5.0.[32] Thus conditions favoring the mechanism proposed in Scheme IC are unlikely to be found in the cytoplasm of microorganisms. Furthermore, there is no conclusive evidence for the existence of the proposed tris(salicylato) $[\mathrm{Fe(H_3\ enterobactin)}]^0$ structure, and formation of such a complex is improbable from stereochemical grounds.

Mechanism B (Scheme I). Since enterobactin precipitates from aqueous acid solutions, Hider and co-workers considered the possible involvement of media having reduced dielectric constants.[14] In living systems, nonaqueous environments are common, for instance, the lipid assemblies associated with membranes and the active sites of many enzymes. Marked changes in pK values can occur in such microenvironments.[33] Thus the observation that protonated tris(catecholato)iron(III) complexes are capable of undergoing internal redox reactions in nonaqueous media may be relevant to the physiological situation. Scheme IB therefore offers a possible mechanism for the reductive release of iron from enterobactin in bacterial cytoplasm.[34-36]

Registry No. Fe, 7439-89-6.

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(31) Pecoraro et al.[19] suggested that only 30% of the iron is in the iron(II) state at pH 4 in their spectra. In their case of dilute solutions, base line curvature can lead to over estimation of the broadened iron(III) component. If the major iron(III) contribution lies in the sharp quadrupole pair rather than the slowly relaxing component, then the percentage of iron(II) has been underestimated. The spectra obtained in concentrated solutions by Hider et al. do not suffer from this problem, so that the iron(II) contribution cannot be derived from a minor impurity; it can in any case be quantitatively converted back to iron(III) enterobactin by neutralization.

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Reactions of Dinuclear Niobium(III) and Tantalum(III) Compounds with Alkyl Isocyanides To Give Dinuclear Products with Dimerized Isocyanides

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Abstract: Reactions of $\mathrm{Nb_2Cl_6(SMe_2)_3}$ and $\mathrm{Ta_2Cl_6(SMe_2)_3}$ with the isocyanides $\mathrm{Me_3CNC}$, $\mathrm{Me_2CHNC}$, and c-$\mathrm{C_6H_{11}NC}$ have been carried out under conditions where the products are all of the composition $\mathrm{M_2Cl_6(RNC)_6}$. All products have been characterized by elemental analyses and IR spectroscopy, and two compounds, $\mathrm{Nb_2Cl_6}(t\text{-}\mathrm{BuNC})_6$ (**1**) and $\mathrm{Ta_2Cl_6}(i\text{-}\mathrm{PrNC})_6$ (**2**), have been further studied by X-ray crystallography. Each of these compounds contains a tetradentate ligand, RNCCNR, formed by dimerization of the isocyanide; this ligand is bonded by its two central carbon atoms to a $\mathrm{MCl_2(CNR)_4}$ group and through its nitrogen atoms to a $\mathrm{MCl_4}$ group. The first metal atom has roughly pentagonal bipyramidal coordination geometry with one Cl and the pair of carbon atoms at apical positions, while the second metal atom has essentially octahedral coordination geometry with the nitrogen atoms in cis positions. Crystallographic results are as follows. For **1**: Pn; $a = 14.102$ (2) Å, $b = 13.486$ (5) Å, $c = 11.157$ (4) Å, $\beta = 93.26$ (2)°, $V = 2118$ (1) Å^3, $Z = 2$, $R_1 = 0.0543$, $R_2 = 0.0727$. For **2**: $P2_1/c$; $a = 18.014$ (8) Å, $b = 11.862$ (4) Å, $c = 17.948$ (5) Å, $\beta = 98.23$ (3)°, $V = 3796$ (4) Å^3, $Z = 4$, $R_1 = 0.0621$, $R_2 = 0.0741$. The compounds are diamagnetic, and this is explained by using an MO scheme that leads to the occupation of a delocalized π MO by both of the metal d electrons.

The ability of the $\mathrm{M_2Cl_6(SR_2)_3}$ molecules (M = Nb or Ta and $\mathrm{SR_2} = \mathrm{SMe_2}$ or $\mathrm{SC_4H_8}$) to react with C≡C and C≡N bonds has been well documented. Often these reactions have included dimerization of the organic ligand so as to form new C—C or C═C bonds.

With internal acetylenes, $\mathrm{R_1C{\equiv}CR_2}$, where $\mathrm{R_1 = R_2 = C_6H_5}$ or $\mathrm{C(CH_3)_3}$ and $\mathrm{R_1 = C(CH_3)_3}$, $\mathrm{R_2 = CH_3}$, simple mono- or diacetylene adducts are formed,[1-4] while terminal acetylenes are catalytically cyclotrimerized or polymerized.[5] Nitriles[1,6] and

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phosphine acetylenes are dimerized and incorporated into dinuclear Nb or Ta complexes. These reactions have been found to be general except where they are prevented by steric factors. We have reported in a preliminary communication[8] that another C≡N containing species, *tert*-butyl isocyanide, is also coupled by reaction with $Nb_2Cl_6(SMe_2)_3$. In this process two isocyanide molecules become connected by a covalent bond formed between terminal carbon atoms. The resulting species is a heterocumulene-type ligand *t*-Bu—N═C═C═N—*t*-Bu which then bonds to two metal atoms.

Further studies in this area have shown that this type of reaction is general for alkyl isocyanides. The products that are obtained from reactions between the Nb or Ta complex with several isocyanides are analogous to the previously reported Nb_2Cl_6(*t*-BuNC)$_6$. In this paper we present the results of the study of these isocyanide systems including crystallographic characterization of one tantalum–isocyanide complex and full details of the structure of the niobium compound which was described in the preliminary communication.

Experimental Section

All manipulations and handling of solvents and reactants were carried out under argon by using the standard vacuum line–inert atmosphere techniques. The procedure for the preparation of $M_2Cl_6(SMe_2)_3$, M = Nb, Ta, was based upon the literature method.[9] The isocyanides (*tert*-butyl, *t*-BuNC; isopropyl, *i*-PrNC; cyclohexyl, CyNC) were purchased from Strem Chemicals, Inc., and used as received. Elemental analyses were performed by Galbraith Microanalytical Laboratories. The spectra were recorded with the use of the following instruments: IR, Perkin Elmer 783 spectrophotometer; ^{1}H NMR, Varian XL 200 spectrometer; EPR, X-band Varian E-65 spectrometer.

All preparations were carried out by reacting the $M_2Cl_6(SMe_2)_3$ complex with excess isocyanide (molar ratio at least 1:7).

Preparation of Nb_2Cl_6(RNC)$_6$. To a solution of $Nb_2Cl_6(SMe_2)_3$ (0.58 g, 1 mmol) in 30 mL of toluene, 3 mL of 3 M isocyanide in toluene was added. Alternatively neat isocyanides were used: 0.8 mL of *t*-BuNC, 0.7 mL of *i*-PrNC and 1.0 mL of CyNC).

The solution changed color to green and then slowly to red-brown. As the reaction progressed colored solid (purple with *t*-BuNC and blue with the other two isocyanides) deposited in the flask. After being stirred for 1 day the mixture was filtered and the solid product washed with toluene and then hexane. The yields of the Nb_2Cl_6(RNC)$_6$ complexes were 60% or greater.

Anal. Calcd for $Nb_2Cl_6(C_4H_9NC)_6$: Cl, 23.77; C, 40.02; N, 9.37; H, 6.03. Found: Cl, 23.6; C, 40.0; N, 9.17; H, 6.25. Calcd for $Nb_2Cl_6(C_6H_{11}NC)_6$: Cl, 20.22; C, 47.86, N, 7.98; H, 6.27. Found: Cl, 19.9; C, 48.7; N, 7.98; H, 6.79.

IR Spectra (KBr disk, cm^{-1}). Nb_2Cl_6(*t*-BuNC)$_6$: 2930 (vs, br), 2220 (s), 1625 (s, br), 1547 (m), 1470 (s), 1449 (s), 1390 (w), 1360 (vs), 1288 (m), 1228 (s), 1190 (vs, br), 1096 (w), 1027 (m), 946 (m), 920 (m), 842 (m), 790 (m), 710 (m), 663 (vw), 641 (w), 615 (m), 596 (m), 553 (w), 530 (m), 461 (m), 451 (m), 420 (vw, br), 400 (w). **Nb_2Cl_6(CyNC)$_6$:** 2840–2940 (vs, br), 2650 (w), 2220 (s), 1615 (m, br), 1540 (vw), 1530 (vw), 1488 (w), 1430 (vs, br), 1340 (vs, br), 1255 (s), 1235 (m), 1190 (w), 1184 (w), 1145 (m), 1015–1120 (vs, br), 954 (s), 928 (m), 890 (s), 861 (m), 840 (m), 812 (m), 793 (m), 782 (m), 773 (m), 750 (m), 730 (w), 694 (m), 667 (m), 650 (m), 639 (w), 571 (s), 555 (w), 540 (m), 492 (m), 468 (w), 448 (m), 421 (m). **Nb_2Cl_6(*i*-PrNC)$_6$:** 2975 (s), 2920 (s), 2860 (m), 2220 (s), 1615 (m, br), 1530 (vw, br), 1430 (vs, br), 1383 (w), 1362 (s), 1330 (s, br), 1257 (m), 1165 (w), 1146 (m), 1110 (s, br), 1025 (w, br), 938 (m), 900 (m), 850 (m), 805 (w), 773 (m), 695 (vw), 675 (m), 665 (sh), 633 (m), 600 (sh), 590 (m), 575 (sh), 519 (m), 480 (m), 430 (m, br), 415 (m, br).

Preparation of Ta_2Cl_6(*i*-PrNC)$_6$. $Ta_2Cl_6(SMe_2)_3$ (0.84 g, 1 mmol) was reacted with *i*-PrNC under conditions similar to those employed for its Nb analogue. The solution underwent color changes from initial brown through transient blue and green to bright red. After 24 h of stirring, red oily deposits of the product as well as a solution of the same color were obtained. The solvent was removed under vacuum. The residue was redissolved in a small amount of acetonitrile (3-5 mL).

Table I. Crystallogrphic Data for Nb_2Cl_6(*t*-BuNC)$_6$ and Ta_2Cl_6(*i*-PrNC)$_6$

	Nb_2Cl_6(*t*-BuNC)$_6$	Ta_2Cl_6(*i*-PrNC)$_6$
formula	$Nb_2Cl_6N_6C_{30}H_{54}$	$Ta_2Cl_6N_6C_{24}H_{42}$
formula wt	897.34	995.26
space group	*Pn*	$P2_1/c$
systematic absences	$h0l$, $h + l \neq 2n$	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
a, Å	14.102 (2)	18.014 (8)
b, Å	13.486 (5)	11.862 (4)
c, Å	11.157 (4)	17.948 (5)
β, deg	93.26 (2)	98.23 (3)
V, Å^3	2118 (1)	3796 (4)
Z	2	4
d_{calcd}, g/cm^3	1.407	1.742
crystal size, mm	0.9 × 0.5 × 0.2	0.5 × 0.5 × 0.07
μ(Mo Kα), cm^{-1}	9.262	61.444
data collection instrument	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
orientation refln, no., range (2θ)	15, $18.63 \leq 2\theta \leq 24.05$	15, $20.23 \leq 2\theta \leq 26.33$
temp, °C	22	5
scan method	ω–2θ	ω–2θ
data col. range, 2θ, deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$
no. of unique data, total	2467	3235
with $F_o^2 > 3\sigma(F_o^2)$	2438	2706
no. of parameters refined	392	286
trans. factors: max, min.	0.9995, 0.9412	0.9997, 0.6429
R^a	0.0543	0.0621
$R_w{}^b$	0.0727	0.0741
quality of fit indicator^c	1.797	1.480
largest shift/esd, final cycle	0.35	0.10

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)^2$. ^{c}Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Addition of Et_2O caused the precipitation of red microcrystalline material, which was filtered, washed with Et_2O, and dried. Yields between 60 and 75% were obtained.

Anal. Calcd for Ta_2Cl_6(*i*-PrNC)$_6$: Cl, 21.54; C, 29.12; N, 8.49; H, 4.25. Found: Cl, 19.9; C, 29.6; N, 7.86; H, 4.32.

IR Spectrum: 2970 (s), 2920 (s), 2855 (m), 2220 (s), 1620 (m, br), 1540 (vw, br), 1455 (m), 1440 (m), 1405 (m), 1381 (m), 1363 (m), 1355 (m), 1328 (s), 1300 (m), 1255 (w), 1157 (m), 1125 (sh), 1110 (s), 1050 (w, br), 1000 (w), 952 (m), 897 (m), 850 (m), 800 (sh), 771 (m), 691 (w), 679 (w), 665 (w), 645 (w), 579 (m), 518 (m), 490 (w), 460 (vw), 421 (w), 410 (vw), 400 (w).

The reactions of *t*-BuNC and CyNC with $Ta_2Cl_6(SMe_2)_3$ were quite similar to that with *i*-PrNC.

The M_2Cl_6(RNC)$_6$ complexes are readily soluble in acetonitrile, THF, CH_2Cl_2, and $CHCl_3$. They do not dissolve in hydrocarbon solvents nor in Et_2O. The combination of acetonitrile and Et_2O was found to be convenient for recrystallization. X-ray quality crystals of Nb_2Cl_6(*t*-BuNC)$_6$ were obtained by cooling the saturated solution in CH_3CN/Et_2O (3:10 v/v) to -5 °C. Occasionally impurities interferred with crystallization, and the best results were obtained when the solid was first washed with the solvent mixture and the second extract used for crystal growth. Crystalline Ta_2Cl_6(*i*-PrNC)$_6$ was obtained by layering its acetonitrile solution with Et_2O.

X-ray Crystallographic Procedure. The crystal structures of Nb_2Cl_6(*t*-BuNC)$_6$ and Ta_2Cl_6(*i*-PrNC)$_6$ were determined by application of general procedures which have been previously described elsewhere.[10] The crystallographic parameters and basic information about data collection and structure refinement are summarized in Table I. Polarization, Lorentz, empirical absorption, and anisotropic decay corrections were applied to the intensity data.

Both structures were solved on the basis of three-dimensional Patterson functions. All non-hydrogen atoms were located and refined by an alternating sequence of difference Fourier analyses and least-squares refinements. Following assignment of anisoptropic thermal parameters to selected atoms (see Tables II and III), the structures were refined to

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Table II. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Nb_2Cl_6(t\text{-}BuNC)_6$

atom	x	y	z	B, Å^2
Nb(1)	0.000	0.19923 (9)	0.000	2.57 (2)
Nb(2)	−0.2596 (1)	0.3518 (1)	0.0120 (2)	3.71 (3)
Cl(1)	0.0615 (3)	0.2230 (3)	−0.1997 (3)	4.52 (9)
Cl(2)	0.1377 (3)	0.0907 (3)	0.0648 (4)	4.42 (9)
Cl(3)	−0.3201 (4)	0.4813 (4)	0.1365 (5)	6.7 (1)
Cl(4)	−0.2316 (3)	0.2597 (4)	0.1938 (4)	5.7 (1)
Cl(5)	−0.4231 (3)	0.2919 (5)	0.0059 (6)	7.6 (2)
Cl(6)	−0.3066 (3)	0.4562 (4)	−0.1574 (4)	5.4 (1)
N(1)	−0.1292 (8)	0.4120 (8)	0.013 (1)	3.3 (2)
N(2)	−0.2293 (8)	0.243 (1)	−0.108 (1)	3.9 (3)
N(3)	−0.1157 (9)	0.0343 (9)	0.166 (1)	4.1 (3)
N(4)	0.0305 (8)	0.254 (1)	0.292 (1)	3.5 (3)
N(5)	0.1889 (8)	0.3584 (9)	0.026 (1)	3.6 (3)
N(6)	−0.037 (1)	−0.0196 (9)	−0.147 (1)	4.4 (3)
C(11)	−0.093 (1)	0.320 (1)	0.003 (1)	3.6 (3)
C(12)	−0.069 (1)	0.503 (1)	0.024 (2)	4.2 (4)
C(13)	−0.009 (1)	0.507 (1)	−0.092 (2)	6.0 (5)
C(14)	−0.008 (2)	0.499 (1)	0.144 (2)	5.9 (5)
C(15)	−0.135 (1)	0.596 (1)	0.025 (2)	6.5 (5)
C(21)	−0.140 (1)	0.239 (1)	−0.056 (1)	2.8 (3)
C(22)	−0.268 (1)	0.172 (1)	−0.198 (2)	5.0 (4)
C(23)	−0.361 (2)	0.216 (2)	−0.263 (2)	7.6 (6)
C(24)	−0.288 (1)	0.078 (2)	−0.141 (2)	6.6 (5)
C(25)	−0.193 (2)	0.163 (2)	−0.300 (2)	6.4 (5)
C(31)	−0.079 (1)	0.092 (1)	0.114 (1)	3.8 (3)
C(32)	−0.167 (1)	−0.040 (1)	0.232 (2)	6.2 (4)
C(33)	−0.183 (3)	0.003 (4)	0.355 (4)	7 (1)*
C(34)	−0.242 (5)	−0.089 (5)	0.150 (6)	11 (2)*
C(35)	−0.129 (4)	−0.141 (4)	0.203 (5)	9 (1)*
C(33A)	−0.101 (5)	−0.074 (5)	0.337 (6)	11 (2)*
C(34A)	−0.174 (5)	−0.141 (5)	0.150 (6)	11 (2)*
C(35A)	−0.267 (4)	−0.016 (4)	0.196 (5)	8 (1)*
C(41)	0.017 (1)	0.240 (1)	0.193 (1)	3.0 (3)
C(42)	0.040 (1)	0.265 (1)	0.425 (1)	3.9 (3)
C(43)	0.146 (1)	0.275 (2)	0.460 (2)	6.6 (5)
C(44)	−0.011 (2)	0.361 (2)	0.458 (2)	8.5 (6)
C(45)	−0.008 (2)	0.175 (2)	0.471 (2)	11.2 (7)
C(51)	0.121 (1)	0.313 (1)	0.024 (2)	3.8 (3)
C(52)	0.276 (1)	0.417 (1)	0.009 (2)	4.3 (4)
C(53)	0.322 (1)	0.376 (2)	−0.100 (2)	7.4 (5)
C(54)	0.246 (2)	0.523 (1)	−0.008 (3)	8.2 (6)
C(55)	0.340 (2)	0.398 (2)	0.121 (2)	6.6 (5)
C(61)	−0.032 (1)	0.057 (1)	−0.100 (1)	3.3 (3)
C(62)	−0.045 (2)	−0.114 (1)	−0.216 (2)	6.5 (5)
C(63)	0.035 (2)	−0.178 (2)	−0.161 (3)	8.9 (7)
C(64)	−0.137 (2)	−0.159 (2)	−0.191 (3)	9.7 (8)
C(65)	−0.044 (3)	−0.087 (2)	−0.346 (2)	13 (1)

[a] Asterisked atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta^{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

convergence. The following are additional comments pertaining to the individual crystal structure determinations.

$Nb_2Cl_6(t\text{-}BuNC)_6$. From systematic absences ($h0l$, $h + l = 2n + 1$) the cell was found to be in a nonstandard setting, *Pn*. Since the transformation to *Pc* would result in a very obtuse β angle, the initial cell was retained.

Among the six *tert*-butyl groups present one was found to be disordered. It refined best with one-half occupancy of the methyl carbon atoms in each of two sets of positions. For the final refinement, all atoms except the disordered ones were assigned anisotropic thermal parameters. The largest peak in the last difference Fourier map had an intensity equal to 0.94 e/Å^3.

$Ta_2Cl_6(i\text{-}PrNC)_6$. We attribute the higher than normal thermal parameters of all atoms to decomposition of the compound during data collection (40% loss of intensity) and significant variation of absorption (minimum transmission was 40%). The latter problem could not be eliminated since the crystals consistently grew in the form of thin plates. The isopropyl groups seemed somewhat disordered as indicated by the values of thermal parameters of their methyl carbon atoms and the presence of residual electron density around them. However, since this disorder was moderate and limited to the less important parts of the molecule, it was disregarded. For only one isocyanide, which was the most severe case, was the disorder included in the refinement. The fractional occupancy of atoms was determined by trail and error and the following values were finally assigned: C(53), 0.7; C(54), 0.3; C(55), 0.4; C (56), 0.6. All methyl carbon atoms were refined isotropically. While the final difference Fourier map revealed some residual electron density (1–2 e/Å^3) located close to the Ta atoms (less than 1.7 Å away) there were, in general, no peaks of chemical significance present in the map.

Table III. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Ta_2Cl_6\ (i\text{-}PrNC)_6$

atom	x	y	z	B, Å^2
Ta(1)	−0.29679 (6)	0.54929 (8)	−0.09568 (5)	4.41 (2)
Ta(2)	−0.18364 (7)	0.31726 (9)	0.06044 (5)	5.18 (2)
Cl(1)	−0.4294 (4)	0.5381 (7)	−0.0790 (4)	8.1 (2)
Cl(2)	−0.3261 (4)	0.6976 (5)	−0.1931 (4)	6.8 (2)
Cl(3)	−0.1036 (5)	0.3347 (6)	0.1801 (4)	8.5 (2)
Cl (4)	−0.0876 (4)	0.4091 (6)	0.0062 (4)	7.1 (2)
Cl(5)	−0.1218 (4)	0.1342 (5)	0.0524 (4)	6.8 (2)
Cl(6)	−0.2683 (5)	0.2142 (6)	0.1279 (4)	8.1 (2)
N(1)	−0.238 (1)	0.459 (2)	0.0816 (9)	5.8 (5)
N(2)	−0.244 (1)	0.287 (1)	−0.041 (1)	6.0 (5)
N(3)	−0.167 (1)	0.480 (1)	−0.2052 (9)	4.6 (4)
N(4)	−0.140 (1)	0.706 (1)	−0.0614 (9)	4.6 (4)
N(5)	−0.332 (2)	0.774 (2)	0.008 (1)	8.3 (7)
N(6)	−0.391 (1)	0.395 (2)	−0.234 (1)	6.1 (5)
C(11)	−0.257 (1)	0.474 (2)	0.009 (1)	3.9 (5)
C(12)	−0.251 (2)	0.539 (3)	0.144 (1)	8.9 (9)
C(13)	−0.194 (2)	0.626 (3)	0.155 (2)	11 (1)*
C(14)	−0.329 (2)	0.540 (4)	0.149 (2)	13 (1)*
C(21)	−0.259 (1)	0.391 (2)	−0.046 (1)	4.9 (5)
C(22)	−0.267 (2)	0.205 (3)	−0.102 (2)	10 (1)
C(23)	−0.195 (2)	0.189 (3)	−0.143 (2)	11 (1)*
C(24)	−0.295 (3)	0.101 (4)	−0.080 (2)	14 (1)*
C(31)	−0.212 (1)	0.501 (2)	−0.170 (1)	4.7 (5)
C(32)	−0.107 (1)	0.459 (2)	−0.250 (1)	6.2 (6)
C(33)	−0.040 (2)	0.411 (3)	−0.197 (2)	8.1 (7)*
C(34)	−0.088 (2)	0.573 (3)	−0.284 (2)	9.0 (8)*
C(41)	−0.188 (1)	0.656 (2)	−0.070 (1)	4.4 (5)
C(42)	−0.076 (2)	0.771 (2)	−0.055 (1)	6.2 (7)
C(43)	−0.091 (2)	0.875 (3)	−0.112 (2)	9.0 (8)*
C(44)	−0.055 (2)	0.813 (3)	0.030 (2)	7.8 (7)*
C(51)	−0.320 (2)	0.700 (2)	−0.023 (1)	7.1 (7)
C(52)	−0.361 (3)	0.881 (4)	0.046 (3)	15 (1)*
C(53)	−0.303 (3)	0.905 (4)	0.111 (2)	9 (1)*
C(54)	−0.371 (6)	0.835 (9)	0.121 (5)	8 (3)*
C(55)	−0.444 (8)	0.94 (1)	0.010 (8)	19 (5)*
C(56)	−0.443 (5)	0.826 (7)	0.070 (4)	14 (2)*
C(61)	−0.357 (1)	0.441 (2)	−0.188 (1)	5.0 (5)
C(62)	−0.442 (2)	0.333 (3)	−0.296 (2)	9.6 (9)
C(63)	−0.451 (3)	0.209 (4)	−0.269 (3)	15 (2)*
C(64)	−0.515 (3)	0.402 (4)	−0.310 (2)	14 (1)*

[a] Asterisked atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta^{13} + bc(\cos\alpha)\beta_{23}]$.

Tables of observed and calculated structure factors and anisotropic thermal parameters, *B*'s, are provided in the supplementary material.

Results and Discussion

Molecular Structures. The atomic positional and equivalent isotropic thermal parameters for the $Nb_2Cl_6(t\text{-}BuNC)_6$ and $Ta_2Cl_6(i\text{-}PrNC)_6$ molecules are listed in Tables II and III, respectively. Important interatomic distances and angles for both compounds are presented in Tables IV and V, respectively. Complete listings of bond distances and angles are included in the supplementary material.

The molecule of $Nb_2Cl_6(t\text{-}BuNC)_6$ is represented by its ORTEP drawing in Figure 1. The tantalum complex is similar, and an analogous atom-labeling scheme has been adopted. The values of bond distances and angles, which are compiled in Tables IV and V, show that there are no significant structural differences between the Nb and Ta compounds. These dinuclear molecules possess a virtual mirror plane which incorporates both metal centers and four chloride ligands (Cl(1), Cl(2), Cl(4), and Cl(6)). The metal atoms are ca. 4.2 Å apart, which rules out the possibility of direct interaction between them. The integrity of the dimer is maintained by a bridge consisting of two isocyanide ligands, which are covalently bound through the terminal carbon atoms.

Table IV. Important Interatomic Distances (Å) for the $M_2Cl_6(RNC)_6$ Complexes, M = Nb, R = *t*-Bu and M = Ta, R = *i*-Pr[a]

	M = Nb	M = Ta
M(1)-M(2)	4.208 (1)	4.236 (1)
M(1)-Cl(1)	2.458 (3)	2.452 (6)
M(1)-Cl(2)	2.504 (3)	2.483 (5)
M(1)-C(11)	2.093 (13)	2.11 (2)
M(1)-C(21)	2.106 (11)	2.15 (2)
M(1)-C(31)	2.257 (13)	2.24 (2)
M(1)-C(41)	2.226 (13)	2.32 (2)
M(1)-C(51)	2.299 (14)	2.28 (2)
M(1)-C(61)	2.259 (13)	2.25 (2)
M(2)-Cl(3)	2.417 (4)	2.418 (6)
M(2)-Cl(4)	2.391 (4)	2.369 (6)
M(2)-Cl(5)	2.440 (4)	2.454 (5)
M(2)-Cl(6)	2.419 (4)	2.411 (6)
M(2)-N(1)	2.010 (9)	2.01 (2)
M(2)-N(2)	2.050 (11)	2.01 (2)
M(2)-C(11)	2.394 (13)	2.39 (2)
M(2)-C(21)	2.421 (11)	2.35 (2)
N(1)-C(11)	1.35 (2)	1.31 (2)
N(2)-C(21)	1.361 (14)	1.26 (2)
N(3)-C(31)	1.12 (2)	1.13 (2)
N(4)-C(41)	1.122 (14)	1.05 (2)
N(5)-C(51)	1.13 (2)	1.08 (2)
N(6)-C(61)	1.151 (15)	1.10 (2)
C(12)-N(1)	1.49 (2)	1.51 (3)
C(22)-N(2)	1.47 (2)	1.48 (3)
C(11)-C(21)	1.42 (2)	1.40 (2)

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

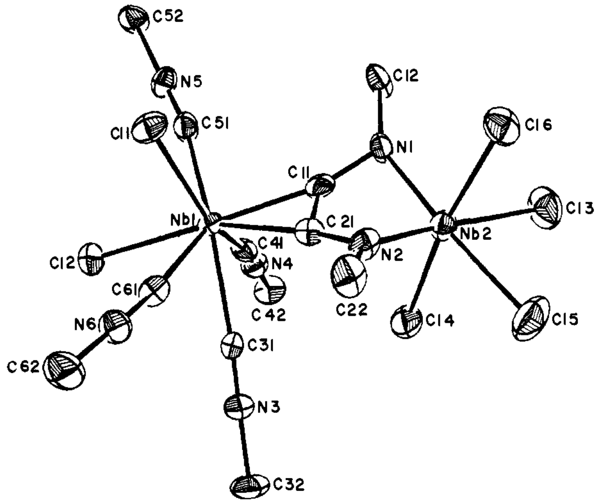
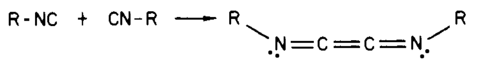


Figure 1. An ORTEP drawing of the $Nb_2Cl_6(t\text{-}BuNC)_6$ molecule. Thermal ellipsoids enclose 30% of the electron density. Methyl carbon atoms have been omitted for the sake of clarity. The $Ta_2Cl_6(i\text{-}PrNC)_6$ complex looks similar and an analogous atom labeling is applicable.

The nature of this bis-isocyanide moiety and its complete structural and electronic role in connecting the two metal atoms is the feature of greatest interest in these compounds.

We have no mechanistic information on how this bridging ligand arises, but in a purely formal sense we may begin with the molecule **1** that would result merely from the appropriate coupling of two isonitrile molecules:



$$\text{R-NC} + \text{CN-R} \longrightarrow \text{R-}\ddot{N}{=}C{=}C{=}\ddot{N}\text{-R}$$

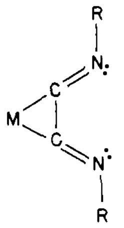
1

A molecule of type **1** is a heterocumulene in which the NCCN unit should be essentially linear. A molecular of type **1** is a heterocumulene in which the NCCN unit should be essentially linear. The π orbitals in the C=N bonds should be perpendicular to the plane of the drawing and the C=C π orbital should be in the plane of the drawing. If a suitable Lewis acid (e.g., a metal ion) approaches the midpoint of the C=C bond, in the plane of the drawing, bonding between the olefin moiety and the metal ion can occur, and under suitable conditions the limiting situation represented in **2** could be approached. The entire entity represented in **2** should ideally be planar. Bending at the two carbon atoms would lead to a situation in which the two lone pairs on the nitrogen atoms should be properly oriented to allow chelation of **2** to another metal ion, thus giving rise to **3**. This, in the simplest possible terms, is the way we propose to look at the construction of the molecules reported here. For the present we shall discuss

Table V. Bond Angles (deg) for $M_2Cl_6(RNC)_6$ Complexes, M = Nb, R = *t*-Bu and M = Ta, R = *i*-Pr[a]

	M = Nb	M = Ta
Cl(1)-M(1)-Cl(2)	91.7 (1)	90.6 (2)
Cl(1)-M(1)-C(11)	99.7 (3)	94.7 (5)
Cl(1)-M(1)-C(21)	94.2 (3)	99.3 (6)
Cl(1)-M(1)-C(31)	143.4 (4)	144.9 (5)
Cl(1)-M(1)-C(41)	145.3 (3)	144.5 (5)
Cl(1)-M(1)-C(51)	73.7 (4)	73.2 (7)
Cl(1)-M(1)-C(61)	74.5 (3)	71.6 (6)
Cl(2)-M(1)-C(11)	157.9 (4)	159.4 (5)
Cl(2)-M(1)-C(21)	158.9 (3)	159.0 (6)
Cl(2)-M(1)-C(31)	82.0 (3)	82.0 (5)
Cl(2)-M(1)-C(41)	80.0 (3)	81.0 (5)
Cl(2)-M(1)-C(51)	78.3 (3)	78.9 (6)
Cl(2)-M(1)-C(61)	77.1 (3)	81.7 (5)
C(11)-M(1)-C(21)	39.4 (5)	38.5 (6)
C(11)-M(1)-C(31)	99.2 (4)	104.2 (7)
C(11)-M(1)-C(41)	79.8 (5)	83.1 (7)
C(11)-M(1)-C(51)	86.7 (5)	83.6 (7)
C(11)-M(1)-C(61)	124.1 (5)	118.8 (7)
C(21)-M(1)-C(31)	81.2 (4)	79.2 (7)
C(21)-M(1)-C(41)	105.6 (4)	100.5 (7)
C(21)-M(1)-C(51)	122.8 (4)	121.6 (8)
C(21)-M(1)-C(61)	85.0 (4)	83.9 (7)
C(31)-M(1)-C(41)	69.1 (5)	68.2 (7)
C(31)-M(1)-C(51)	138.5 (5)	137.4 (8)
C(31)-M(1)-C(61)	69.0 (5)	73.4 (7)
C(41)-M(1)-C(51)	71.6 (5)	71.3 (9)
C(41)-M(1)-C(61)	134.3 (4)	139.6 (7)
C(51)-M(1)-C(61)	138.8 (4)	139.3 (9)
Cl(3)-M(2)-Cl(4)	86.3 (2)	87.0 (2)
Cl(3)-M(2)-Cl(5)	83.8 (2)	84.8 (2)
Cl(3)-M(2)-Cl(6)	86.5 (2)	86.4 (3)
Cl(3)-M(2)-N(1)	93.3 (3)	90.2 (5)
Cl(3)-M(2)-N(2)	170.7 (3)	173.5 (5)
Cl(4)-M(2)-Cl(5)	87.8 (2)	91.0 (2)
Cl(4)-M(2)-Cl(6)	171.7 (1)	172.4 (2)
Cl(4)-M(2)-N(1)	95.6 (3)	95.5 (5)
Cl(4)-M(2)-N(2)	98.9 (3)	92.5 (5)
Cl(5)-M(2)-Cl(6)	87.4 (2)	84.6 (6)
Cl(5)-M(2)-N(1)	175.3 (3)	171.6 (4)
Cl(5)-M(2)-N(2)	88.7 (3)	88.7 (4)
Cl(6)-M(2)-N(1)	88.9 (3)	88.3 (5)
Cl(6)-M(2)-N(2)	87.8 (3)	93.6 (6)
N(1)-M(2)-N(1)	93.9 (4)	96.2 (6)
M(1)-C(11)-N(1)	163 (1)	162 (1)
M(1)-C(11)-C(21)	70.8 (8)	72.3 (9)
M(1)-C(21)-N(2)	165.1 (9)	160 (2)
M(1)-C(21)-C(11)	69.8 (7)	69 (1)
M(2)-N(1)-C(11)	88.6 (7)	90 (1)
M(2)-N(1)-C(12)	148.4 (7)	143 (2)
C(11)-N(1)-C(12)	123 (1)	127 (2)
M(2)-N(2)-C(21)	88.0 (7)	88 (1)
M(2)-M(2)-C(22)	146.4 (8)	148 (2)
C(21)-N(2)-C(22)	124 (1)	123 (2)
M(1)-C(31)-N(3)	176 (1)	177 (2)
M(1)-C(41)-N(4)	174 (1)	177 (4)
M(1)-C(51)-N(5)	169 (1)	176 (2)
M(1)-C(61)-N(6)	171 (1)	174 (2)
C(31)-N(3)-C(32)	178 (2)	177 (2)
C(41)-N(4)-C(42)	174 (1)	177 (2)
C(51)-N(5)-C(52)	171 (1)	172 (3)
C(61)-N(6)-C(62)	175 (1)	176 (2)

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



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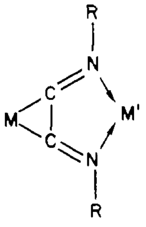
the structural results in terms of this picture, but later it will be shown that this simple concept must be further elaborated to provide a satisfactory account of all the experimental facts.



3

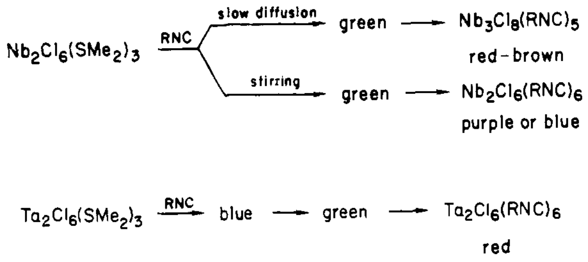
We observe that each metal center in the reported compounds has a different coordination geometry. M(1) can be considered to have pentagonal bipyramidal coordination if the C(11)–C(21) moiety is regarded as one ligand occupying an axial site. The other axial site is occupied by Cl(2), and the five equatorial ligands are Cl(1) and the four RNC groups that retain their identities as such. The two M(1)–Cl distances are slightly different, but both are longer than those to the other metal atom, in keeping with the higher coordination number of M(1). The C–N–C–M(1) groups of the four equatorial isocyanide ligands are all effectively linear. The M–C–N angles are in the range 169 (1)° to 176 (1)° while the C–N–C angles are in the range 171 (1)° to 178 (1)°.

The other metal atom, M(2), has distorted octahedral coordination. The metal–chlorine bonds trans to the Nb–N bonds have an average length of 2.429 [9] Å while those bonds to the other chlorine atoms have an average length of 2.405 [10] Å. The difference, 0.024 (13) Å, is not statistically significant, nor is there any significant difference in the tantalum case. The cis Cl–M–Cl angles range from 83.8° to 91.0°. The N–M–N angles are 94.9 (4)° and 96.2 (6)° for the Nb and Ta compounds, respectively. It would appear that the pattern of distortions from regular octahedral angles is simply that expected from the large bite of the diamine ligand.

Let us return now to a more detailed consideration of the structure of the bridging ligand. As idealized in **3** it would be a 1,4-diazabutadiene, or 1,2-diiminoethane ligand, which is a type of ligand that has been extensively investigated in recent years by the Amsterdam inorganic research group.[11] This idealization is a bit of an oversimplification, however. In a true 1,4-diazabutadiene ligand such as that found[11] in $PtCl_2(\eta^2\text{-styrene})(t\text{-Bu—N=CHCH=N—}t\text{-Bu})$, the C–N distances are short, ca. 1.28 Å, indicative of essentially localized double-bond character, and the C–C distance, 1.51 (5) Å, is consistent with essentially single-bond character. In our compounds, however, the C–N distances are somewhat longer, averaging 1.32 Å, while the C–C distances, 1.40 and 1.42 Å, are shorter. Admittedly, the uncertainties in all individual values, both in our compounds and the platinum compound, are large enough to blur the issue, but it does appear that π delocalization is significant in the niobium and tantalum compounds, whereas it is perhaps negligible in the platinum compound.

One final structural observation concerns the nonplanarity of the central $M(1)C_2N_2R_2M(2)$ unit. In the idealization represented by **3**, this entire set of atoms would lie in the same plane. In fact, the $M(1)C_2N_2$ set of atoms is essentially planar in each case, but there is a dihedral bend along the N(1)···N(2) line, with M(2) lying below this mean plane (by 0.92 Å, 0.66 Å for Nb and Ta, respectively) and the carbon atoms C(12) and C(22) lying a little above the plane (an average of 0.43 Å for all four). The dihedral angles themsevles are 42.8° and 30.3° for the niobium and tantalum compounds, respectively. We propose that these deviations from complete planarity are the result of nonbonded interactions, such as repulsive forces between the *tert*-butyl groups on N(1) and N(2) and chlorine atoms Cl(3) and Cl(5), rather than indications that there is any feature in the bonding that drives the system away from planarity.

Scheme I



Reactions and Spectra. The Nb^{III} and Ta^{III} confacial bioctahedral dimers were allowed to react with three alkyl isocyanides and in each case, independent of the R group, the system behaved as shown in Scheme I.

The transient stages are very distinct, indicating formation of well-defined intermediate species. In the case of Ta the intermediates can be isolated as stable products when less isocyanide is used. Thus the blue compound is obtained with 2–3 equiv of isocyanide per dimer, and with about 4 equiv the green material can be isolated. The intermediates are apparently Nb or Ta complexes with a coordination sphere partially filled with RNC ligands. A noteworthy feature of the Nb system is that upon slow mixing of reactants by diffusion the trimeric complex can be isolated while with Ta the same dinuclear compound is always obtained.

Although there is some degree of dissimilarity between the reactions of Nb and Ta, viz., one vs. two distinct intermediates, in both cases an identical final product is obtained, namely $M_2Cl_6(RNC)_6$. Apart from elemental analyses and crystallographic determinations, an independent verification of that is provided by IR spectra. They are essentially identical for the four complexes studied in the region where the stretching vibrations of the isocyanide group[12] are observed, roughly 1600–2500 cm^{-1}. Only two bands are seen there; one is a strong sharp band at 2220 cm^{-1} and the other is a medium or strong band at ca. 1620 cm^{-1}. The former may be assigned to N≡C stretches of the terminal isocyanide ligands. As expected for RNC bonded to a metal ion, there is a shift to higher energy with respect to the free ligand. We believe that the band at 1620 cm^{-1} should be considered in conjunction with a band at about 1540 cm^{-1}, which is distinct for the *t*-BuNC complex and very weak and broad for the other compounds. If the RN=C—C=NR system has appreciable π delocalization, two ν(C—N) modes, symmetric and antisymmetric, should be seen in the infrared spectrum. If the two observed bands are so assigned, their average frequency, about 1580 cm^{-1}, compares properly with (i.e., it is less than) that in the platinum compound discussed earlier, where a single band is reported at 1603 cm^{-1}.

Proton NMR spectra of the isocyanide species indicate that there is complex behavior in solution. Variable-temperature measurements (-18.9 to 40 °C) for $Nb_2Cl_6(t\text{-BuNC})_6$ in $CDCl_3$ showed that both fluxional and equilibrium processes are probably involved. At +40 °C two major signals are observed: at 1.821 ppm (A) and 1.518 ppm (B) with an intensity ratio of roughly 1:2. They may be assigned to the bridging and terminal isocyanides, respectively, with the latter undergoing rapid exchange

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(11) van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.*, **1981**, *20*, 2941 and references cited therein.

(12) Malatesta, L.; Bonati, F. "Isonitrile Complexes of Metals"; Wiley: New York, 1969.

over the two nonequivalent sites. Two additional relatively broad and weak resonances are observed at 1.77 ppm (C) and 1.64 ppm (D). As the temperature is lowered to 2.8 °C the intensities of A and C remain essentially constant, while D increases at the expense of B. The latter is a doublet at 22.7 °C (lower field peak somewhat broadened) and a singlet at 2.8 °C. The following are the positions and estimated relative intensities of the resonances at several temperatures: At 22.7 °C; A, 1.809 ppm, 1; B, 1.525 and 1.514 ppm, ~1.6; D, 1.629 ppm, ~0.4. At 2.8 °C: A, 1.827 ppm, 1; B, 1.508 ppm, ~ 1.25; D, 1.631 ppm, ~0.75. At −18.9 °C: C is not observed, A is at 1.809 ppm, D is at 1.627 ppm with a shoulder at 1.617 ppm; B is at 1.499 ppm, and two new signals appear at 1.587 and 1.539 ppm, the latter with two shoulders. The intensity of peaks in the region 1.63 to 1.5 ppm remains twice that for A. Considerations based upon the major peaks only can explain the relative changes of intensity of B and D from 2.8 to 40 °C by a temperature-dependent equilibrium between some two species assuming continuing scrambling of the four terminal isocyanides. If that is the case the rate of exchange between the two is slow on the NMR time scale since no coalescence is observed. The appearance of additional signals at −18.9 °C may be due to the loss of fluxionality of the terminal ligands. However, to account for the weaker signals very speculative arguments would have to be proposed, and therefore the matter will not be discussed further. It is possible that the $M_2Cl_6(RNC)_6$ complexes in solution become "locked" in several different conformations, particularly at lower temperatures. The behavior of $Nb_2Cl_6(t\text{-}BuNC)_6$ in CD_3CN is more complex than that in $CDCl_3$ although similar features are observed. The complicating factor is apparently due to partial substitution of RNC ligands by acetonitrile molecules.

In the spectrum of $Nb_2Cl_6(i\text{-}PrNC)_6$ in CD_3CN several heptets (CH groups) and doublets (CH_3 groups) were observed. This indicated a behavior as complex as in the butyl case. Since an isopropyl group gives more resonances than the *tert*-butyl one, the latter complex was chosen for the detailed NMR study (vide supra).

Intermetallic Electron Coupling. The NMR spectra pose some interpretational problems, as just noted, but their chief importance is that they show that the $Nb_2Cl_6(t\text{-}BuNC)_6$ molecule (and presumably its tantalum analogue) is diamagnetic. This conclusion is supported by the lack of any EPR signal for $Nb_2Cl_6(t\text{-}BuNC)_6$ at −196 °C. The best way to account for a lack of unpaired electrons in this molecule will now be considered.

We begin by noting that the bonding of the C(11)–C(21) moiety to the Nb(1) atom according to 3 together with the presence of two chlorine atoms in the coordination sphere of Nb(1) would imply an oxidation number of 4+ for Nb(1). Similarly, for Nb(2) an oxidation number of 4+ also seems reasonable. Naturally, the total oxidation number, 8+, could conceivably be apportioned in some other way, but only the 5+, 3+ or 3+, 5+ assignments seem at all worth considering. We believe that they are unlikely since electron flow through a bridging system would favor equalization of charge on the two metal atoms. However, if there were to be an unequal assignment of oxidation numbers, the metal atom with oxidation number 5+ would be expected to have much shorter Nb–Cl bond lengths (i.e., in the range 2.25–2.30 Å as found in Nb_2Cl_{10}[13]) than those actually found. Thus we shall address the problem of accounting for the diamagnetism of these compounds assuming that we can begin with two 4+ metal atoms. In any event, even if we were to begin with 3+, 5+ or 5+, 3+ assignment, the argument now to be developed would still lead to the same qualitative result.

If we begin with the assumption of two formally 4+ metal ions (d^1 ions) linked by the $C_2N_2R_2$ bridging system, it can be shown straightforwardly that interactions of metal d orbitals with the π system in the $C_2N_2R_2$ unit will naturally lead to a singlet ground state in which the individual, unpaired metal d electrons become part of an overall six-electron π system.

The bridging RN–C–C–NR unit must have a set of π molecular orbitals quite analogous to those of butadiene,[14] the only difference being that the nitrogen atoms will participate more in the two lower energy MO's and the carbon atoms more in the two higher energy MO's. For M(1), the pentagonal bipyramidal arrangement of ligands will tend to send three of the d orbitals (two in the equatorial or x,y plane and the d_{z^2}) to high energies leaving the d electron to occupy one of the $d\pi$ orbitals. Similarly for M(2) the d electron will occupy a $d\pi$-type orbital. One of the $d\pi$ orbitals

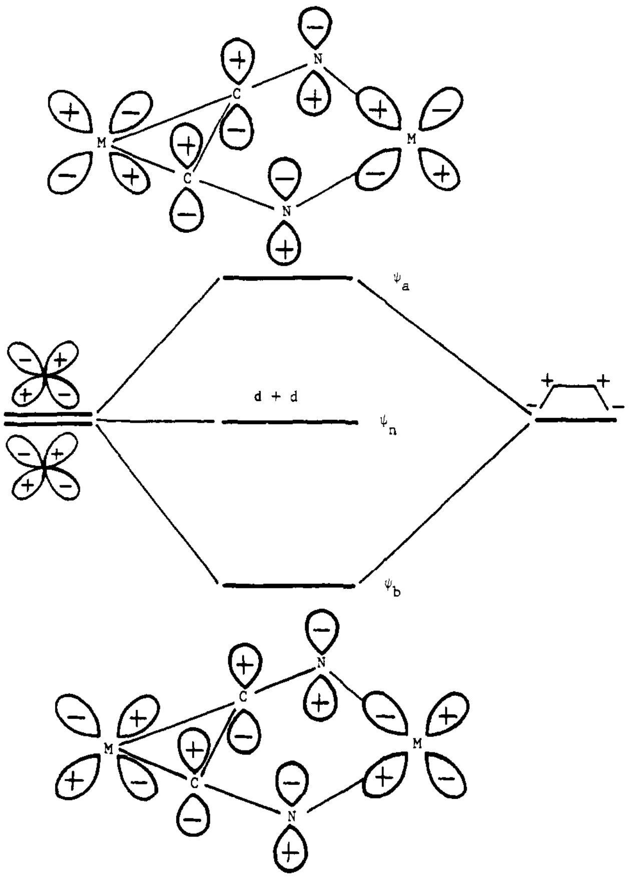

Figure 2. Diagram showing the interaction between two appropriate metal $d\pi$ orbitals and one of the π MO's of the bridging $C_2N_2R_2$ ligand.

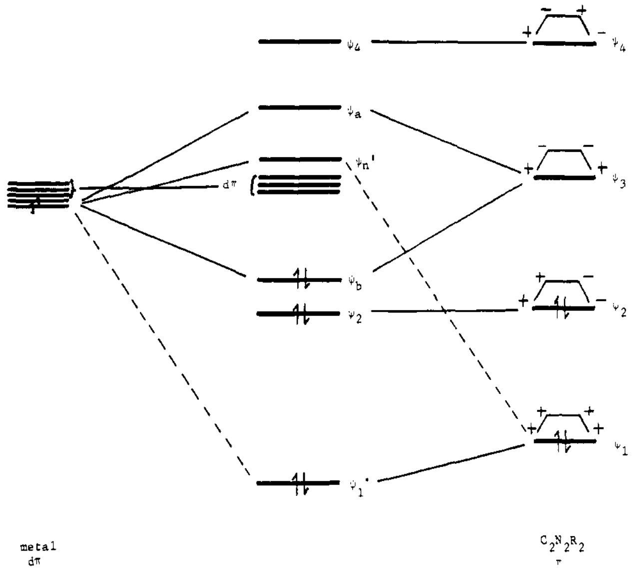

Figure 3. Diagram showing how the entire $M(1)C_2N_2R_2M(2)$ system will develop a π^6 configuration, thus accounting for the "long-range" coupling of spins on two M^{4+} (d^1) metal atoms.

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[13] Zalkin, A.; Sands, D. E. *Acta Crystallogr.* **1958**, *11*, 615.

[14] See any book on elementary organic MO theory, e.g.: Cotton, F. A. "Chemical Applications of Group Theory"; John Wiley and Sons: New York, 1971; p 186.

on each metal atom and the upper A-type π orbital of the RNCCNR group, ψ_3, are permitted by symmetry to interact as shown in Figure 2 to give three MO's, one of which, ψ_b, will be a good bonding orbital for the $M(1)C_2N_2R_2M(2)$ system as a whole. There will also be a corresponding antibonding MO, ψ_a, and an essentially nonbonding MO, ψ_n, made up of the two metal dπ orbitals only.

When these metal–ligand interactions are considered in conjunction with the other π orbitals of the bridging butadiene ligand and the dπ orbitals that are orthogonal to the $C_2N_2R_2$ π orbitals, we get the picture shown in Figure 3. It can be seen that the interaction of the two sets of π orbitals leads to the formation of a singlet π^6 configuration and accounts for the diamagnetism of the molecule. There is a symmetry-permitted interaction between the ψ_n orbital of Figure 2 and the ψ_1 MO of the $C_2N_2R_2$ group which leads to a slight mixing and a slightly increased separation of these orbitals; they are thus shown slightly displaced and are designated ψ_n' and ψ_1' in Figure 3.

Concluding Remarks. Returning again to the question of how these unusual molecules are formed, we do not have any detailed idea. It is significant that the same sort of product can be obtained for both niobium and tantalum. Although transition metals are known to catalyze polymerization[12] of isocyanides this complex-mediated dimerization appears to be unprecendented.[12,15,16] One prior example of such coupling has been reported but under explicitly reductive conditions in the presence of zinc giving η^2-RHNCCNHR bonded to Mo.[17] It is possible that in our case the crucial factor is the presence of the double bonded M═M unit. The same number of chlorine atoms in both the starting complex and the resulting product as well as the high efficiency of the process indicate that the dinuclear unit may not be cleaved into separate mononuclear species. The participation of monomeric intermediates would be expected to give more heterogeneous products.

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Registry No. $Nb_2Cl_6(t\text{-}BuNC)_6$, 85533-79-5; $Nb_2Cl_6(CyNC)_6$, 92078-20-1; $Nb_2Cl_6(i\text{-}PrNC)_6$, 92078-21-2; $Ta_2Cl_6(i\text{-}PrNC)_6$, 92078-19-8; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0; $Ta_2Cl_6(SMe_2)_3$, 77827-59-9.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, *B*'s, complete listing of bond distances and angles, and selected least-squares planes (40 pages). Ordering information is given on any current masthead.

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N,O-Silatropic Rearrangements. Enhanced Silyl Group Exchange between Nitrogen and Oxygen via Chelation to Nickel and X-ray Crystal Structure of a Substituted *N*,*O*-Disilylimidate Moiety

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Abstract: The nickel(II) hydrocarbyl complexes $Ni(R)[N(SiMe_2CH_2PPh_2)_2]$ (R = methyl, allyl, vinyl, and phenyl) react with 1 atm of carbon monoxide at room temperature to generate nickel(0) dicarbonyl derivatives $Ni(CO)_2[RC{=}N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$. Loss of one CO ligand from the vinyl derivative $Ni(CO)_2[C_2H_3C{=}N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$ occurs readily under vacuum to produce a new Ni(0) complex containing an η^2-bonded acryloyl unit. This species, $Ni(CO)[(\eta^2\text{-}C_2H_3)C{=}N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$, has been structurally characterized by X-ray crystallography: space group $P2_1/n$; a = 16.240 (3) Å, b = 11.534 (1) Å, c = 19.076 (3) Å; Z = 4; R = 0.050, R_w = 0.058. The exclusive *N*,*O*-disilylimidate tautomeric form of the diphosphine ligand in all of these complexes was established spectroscopically through ^{15}N labeling and variable-temperature ^1H and ^{29}Si NMR experiments. Rapid silyl group exchange between the nitrogen and oxygen centers occurs with all of these Ni(0) complexes. In fact, comparison of $\Delta G^{\ddagger}$ values for silyl exchange for the uncoordinated acylated disilylphosphine $PhC{=}N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2$ and its Ni(0) derivative indicate a substantial enhancement for this migration when the ligand is bound to Ni; the reason for the enhancement in the rate of silyl group migration is discussed.

Introduction

It has been well documented[2-4] that, except in the case of $HCON(SiMe_3)_2$, all linear bis(trimethylsilyl)amides, $RCON(SiMe_3)_2$ (R = alkyl or aryl), exist predominantly as the *N*,*O*-disilylimidate tautomer **1** rather than as the amide isomer **2**. In addition, all alkyl and aryl amides undergo reversible intramolecular exchange of the trimethylsilyl groups between the nitrogen and oxygen centers. It is generally accepted[3-5] that the mechanism of this silyltropic rearrangement involves rapid, free rotation of

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