Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02154

Crystal and Molecular Structure of $\{Ni[(CH_3)_2C(OH)CH_2COCH_3]_2\}\{Ni[NCS]_4[P(CH_2CH_2CN)_3]_2\}$: A β-Hydroxy Ketone Chelate Complex

BRUCE M. FOXMAN* and HARRY MAZUREK

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The title compound has been synthesized and its crystal structure determined by single-crystal X-ray diffraction methods. The complex crystallizes in space group $P\bar{1}$, with $a = 12.773$ (4) Å, $b = 11.421$ (3) Å, $c = 8.864$ (3) Å, $\alpha = 106.37$ (5)°, $\beta = 78.56$ (5)°, and $\gamma = 104.37$ (5)°. Full-matrix least-squares refinement of positional and thermal parameters for all atoms (three methyl H atoms fixed), with 3610 reflections ($F > 3.92\sigma(F)$) led to $R = 0.044$ and $R_w = 0.064$. Both cation and anion occupy crystallographic centers of symmetry. In the cation, the β-hydroxy ketone ligand is (as expected) not planar: the hydroxyl oxygen atom and β-carbon atom lie +0.40 and −0.38 Å out of a plane containing Ni and the other ligand atoms. The Ni–O distances to the carbonyl and hydroxyl oxygen atoms are 1.895 (3) and 1.927 (3) Å, respectively. The anion is trans octahedral; Ni–N–C angles show large distortions from linearity: 160.7 (3) and 163.9 (3)°.

Introduction

Square-planar nickel(II) complexes of the polyfunctional phosphine ligand tris(2-cyanoethyl)phosphine (hereafter, CEP) undergo a series of interesting solid-state transformations.[1,2] We have endeavored to study such solid-state processes, using CEP, various transition metals (Ni, Pd, Pt, Fe, Co), and halide or pseudohalide anions (F^-, Cl^-, Br^-, I^-, SCN^-). In one of several attempts to synthesize various $Ni(CEP)_2(NCS)_2$ phases, the title complex was formed in very poor yield. Since only a very small amount of the material was available, the most feasible method of analysis was deemed to be a single-crystal X-ray structure determination.

There are numerous examples of transition-metal–oxygen chelate complexes in the chemical literature, particularly acetylacetonate complexes.[3] However, we believe this to be the first reported discovery and X-ray structural characterization of a neutral β-hydroxy ketone, 4-hydroxy-4-methyl-2-pentanone (hereafter diacetone alcohol), acting as a bidentate ligand.

Experimental Section

The crystal used in this study was synthesized by a technique similar to that employed for the syntheses of $NiX_2(CEP)_2$ complexes (X = Cl, Br).[1] Apparently, an aldol condensation occurred during one of the preparations, and a pale yellow-orange material (~100 mg) deposited, instead of the usual product, red $Ni(NCS)_2(CEP)_2$. All attempts to reproduce that preparation, the details of which are available from the authors, invariably failed. Further, attempts to prepare the complex directly from diacetone alcohol, $Ni(NCS)_2$, and CEP led only to $Ni(NCS)_2(CEP)_2$. We have devised a preparation of this elusive material which is relatively reproducible and gives the complex in poor yield.

[Ni(diacetone alcohol)$_2$][Ni(NCS)$_4$(CEP)$_2$]. $Ni(NCS)_2$ (0.50 g, 0.0029 mol, ROC/RIC), CEP (0.44 g, 0.0023 mol, Aldrich), 12 mL of absolute EtOH, 10 mL of reagent grade acetone, 2 mL of triethyl orthoformate, 0.5 mL of *t*-BuOH, and ~10 mg of K(*t*-OBu) are mixed in a 25-mL flask. The flask is kept at −10 °C for 17 h after which time the mixture is poured onto filter paper in a Büchner funnel. The funnel and a tight-fitting vial (to collect the liquid) are placed in a warm (~30 °C) area. After the flocculent precipitate dries to a cake, it is removed, and a small amount of pale yellow-orange crystals is found on the paper. More sophisticated (and intelligent) approaches to the synthesis of this material were attempted, to no avail. The magnetic susceptibility of the complex at 25 °C, $\chi_m^{cor} = 4.23 \times 10^{-3}$ cgsu leads to $\mu = 3.17\ \mu_B$.

Collection and Reduction of Diffraction Data. Preliminary Weissenberg (0*kl*, 1*kl*) and precession (*hk*0, *hk*1, *h*0*l*, *h*1*l*) photographs showed neither systematic absences nor symmetry, leaving space groups $P1$ or $P\bar{1}$ as possible choices; the latter was confirmed by successful refinement of the structure. A Lauë photograph of the crystal indicated it to be of excellent quality, and it was transferred to a Supper No. 455 goniometer and centered optically on a Syntex $P2_1$ diffractometer.

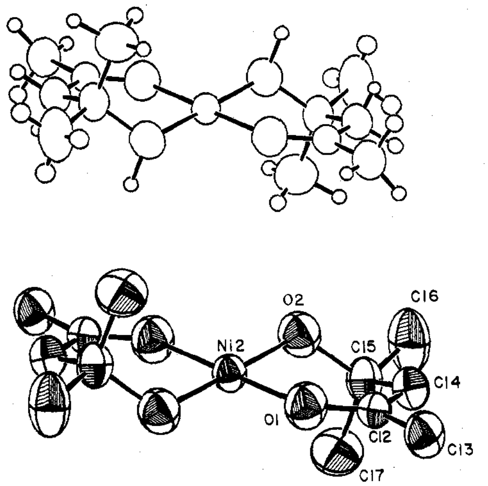

Figure 1. Molecular structure of the $\{Ni[(CH_3)_2C(OH)CH_2COCH_3]_2\}^{2+}$ ion, showing (top) location of all atoms, including hydrogen, and (bottom) 50% probability ellipsoids for atoms refined anisotropically.

Most operations were carried out as described previously;[4] other operations are described below. Details of the structure analysis, in outline form, are presented in Table I.

Solution and Refinement. Initial computational work was carried out on a limited data set with the Brandeis University PDP-10 computer, using local versions of programs described previously.[4,5] The analysis was completed some time later on a Syntex XTL structure determination system (24 K Nova 1200 configuration).[6] The analytical scattering factors of Cromer and Waber were used;[7a] real and imaginary components of anomalous scattering were included in the calculations for all nonhydrogen atoms.[7b] The structure was solved with difficulty from a rather complicated three-dimensional Patterson map. The map had its largest peak at ($^1/_2$, 0, $^1/_2$), and the appearance of peaks (ca. eight) about the latter was similar to the distribution about the origin. It was thus apparent that two independent centers of symmetry were occupied by dissimilar ions. The trial structure was deduced from chemical considerations and the experimentally determined X-ray molecular weight of the unit cell. A trial structure factor calculation using derived coordinates for Ni1, Ni2, and P gave $R = 0.492$. The remaining atomic positional parameters were obtained (with some difficulty due to poor phasing) from successive difference Fourier syntheses. At the conclusion of anisotropic refinement of all nonhydrogen atoms, a difference Fourier synthesis revealed the positions of all hydrogen atoms. These refined successfully except for the methyl hydrogen atoms attached to C16. For these the program METHYL[8] was used to generate tetrahedral positions for the methyl H atoms at 10° intervals about the C15–C16 bond axis. Calculated H atom positions were then selected, which were the "best fit" to the set of three observed H atom positions. These three H atoms (H16A,

Table I. Data for the X-ray Diffraction Study of $\{Ni[(CH_3)_2C(OH)CH_2COCH_3]_2\}\{Ni[NCS]_4[P(CH_2CH_2CN)_3]_2\}$

(A) Crystal Data at 21 (1) °C

crystal system: triclinic[a]
space group: $P\bar{1}$ [C_i^1; No. 2]
$a = 12.773$ (4) Å
$b = 11.421$ (3) Å
$c = 8.864$ (3) Å
$\alpha = 106.37$ (5)°
$\beta = 78.56$ (5)°
$\gamma = 104.37$ (5)°

$V = 1190.3$ Å^3
$Z = 1$
crystal size: 0.16 × 0.20 × 0.24 mm
formula wt = 968.5
ρ(calcd) = 1.351 g cm^{-3}
ρ(obsd)[b] = 1.34 (1) g cm^{-3}
$\mu = 35.0$ cm^{-1} (Cu Kα)

cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ, ω, χ values in the range $50 < |2\theta| < 52°$ (λ(Cu K$\bar{\alpha}$) 1.5418 Å)

(B) Measurement of Intensity Data

radiation: Cu Kα, Ni β filter
reflections measd: $-h,\pm k,\pm l$ (to $2\theta = 101°$)
scan type, speed: θ-2θ, variable, 1.95-4.51°/min
scan range: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
background measurement: stationary, for one-quarter of scan time at each of the scan limits
no. of reflections measd: 5062 total; 4309 in unique set
standard reflections: $06\bar{2}$, 024, $\bar{2}10$, $\bar{7}20$, showed a steady decrease of 6% ($\bar{2}10$) to 15% (others) with time; an isotropic, sin θ-dependent correction was applied[c]
automatic recentering after every 750 reflections

(C) Treatment of Intensity Data[d]

data reduction: intensities as before,[4] esd's of $|F_o|$ values calcd by method of finite differences, after Churchill et al.[e]
statistical information: $R_S = 0.015$ ($I > 1.96\sigma(I)$); $R_{av} = 0.016$ (mainly $0kl$ reflections)

(D) Refinement,[f] with 3610 Data for Which $F > 3.92\sigma(F)$

weighting of reflections: $w = [\sigma^2(|F_o|) + (p|F_o|)^2]^{-1}$; $p = 0.035$
isotropic refinement, all nonhydrogen atoms: $R = 0.116$; $R_w = 0.116$
anisotropic refinement, all nonhydrogen atoms: $R = 0.060$; $R_w = 0.094$
anisotropic refinement as above; isotropic refinement of hydrogen atoms, except three hydrogen atoms attached to C16 included as fixed: $R = 0.044$; $R_w = 0.064$
structure factor calcn, all 4309 data: $R = 0.054$; $R_w = 0.067$
standard deviation of an obsvn of unit weight (SDU): 1.539
final difference Fourier map: 0.73 e/Å^3 near S2; five other peaks ~0.35 e/Å^3 near heavy atoms; remainder: random peaks ≤0.29 e/Å^3

[a] The corresponding primitive Delaunay reduced cell has $a = 12.773$ Å, $b = 12.327$ Å, $c = 8.864$ Å, $\alpha = 117.25°$, $\beta = 101.44°$, and $\gamma = 95.01°$. [b] Measured by flotation in CCl_4-C_6H_6. [c] A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, 90, 6675 (1968). [d] $R_s = \Sigma\sigma(|F_o|)/\Sigma|F_o|$; $R_{av} = [(\Sigma||I| - |I_{av}||)/\Sigma|I|]$. [e] M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, 16, 265 (1977). [f] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$. SDU $= \{\Sigma w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ where m (=3610) is the number of observations and n (=340) is the number of parameters.

B, C) were included, as fixed contributions to F_c (with C–H = 0.95 Å), in subsequent cycles of least-squares refinement. The calculation procedure above was repeated after each cycle of refinement. At convergence, $[(\Delta/\sigma_{max}) \leq 0.09]$, a weighting scheme analysis revealed no systematic dependence of $w[|F_o| - |F_c|]^2$ on $|F_o|$, $(\sin\theta)/\lambda$, parity of indices, or sequence number. Table II lists the positional and isotropic temperature factors for all atoms, while anisotropic temperature factors appear in Table III.

Results and Discussion

$[Ni(diacetone alcohol)_2]^{2+}$. Various features of the molecular structure of the cation, including the location of the ROH hydrogen atom, are depicted in Figure 1. Examination of pertinent bond distances and angles (Table IVA) confirms the formulation of the cation as a bis(β-hydroxy ketone) chelate complex. For this square-planar complex, the shortest intermolecular contact to nickel, Ni2–S2, is 4.09 Å. Features which distinguish this ligand from the closely related, planar acetylacetonate ligand and its complexes are as follows:

Table II. Atomic Coordinates and Isotropic Temperature Factors for $[Ni(diacetone alcohol)_2][Ni(NCS)_4(CEP)_2]$[a]

atom	x	y	z	U_{iso}, Å^2
Ni1	0.00000	0.00000	0.00000	
Ni2	0.50000	0.00000	−0.50000	
P	−0.00885 (6)	0.21850 (7)	0.07827 (8)	
S1	0.37149 (7)	0.00480 (10)	0.02770 (11)	
S2	0.19697 (10)	0.05694 (14)	−0.50258 (12)	
N1	0.16048 (20)	0.03822 (25)	0.04176 (32)	
N2	0.05989 (23)	0.01398 (26)	−0.23013 (32)	
N3	0.30208 (31)	0.43149 (37)	0.42054 (52)	
N4	−0.09845 (33)	0.35596 (33)	−0.38034 (38)	
N5	−0.21954 (32)	0.46551 (38)	0.08935 (52)	
O1	0.52803 (25)	0.11901 (27)	−0.62254 (35)	
O2	0.42448 (25)	0.10722 (27)	−0.32752 (35)	
C1	0.24803 (23)	0.02643 (27)	0.03767 (33)	
C2	0.11562 (26)	0.03153 (30)	−0.34307 (38)	
C3	0.10901 (28)	0.32387 (33)	0.16614 (42)	
C4	0.12313 (32)	0.29610 (40)	0.31974 (43)	
C5	0.22496 (31)	0.37133 (35)	0.37719 (44)	
C6	−0.00934 (28)	0.29034 (32)	−0.08204 (39)	
C7	−0.10167 (31)	0.22540 (35)	−0.18184 (42)	
C8	−0.10117 (30)	0.29635 (33)	−0.29606 (39)	
C9	−0.12889 (27)	0.25195 (29)	0.22222 (36)	
C10	−0.14321 (33)	0.38785 (35)	0.28506 (45)	
C11	−0.18544 (30)	0.43264 (33)	0.17506 (50)	
C12	0.51545 (27)	0.23065 (30)	−0.58791 (42)	
C13	0.53709 (42)	0.30363 (47)	−0.71225 (58)	
C14	0.47343 (37)	0.29655 (37)	−0.42709 (48)	
C15	0.47528 (33)	0.24334 (33)	−0.28767 (43)	
C16	0.40454 (55)	0.30789 (48)	−0.14187 (57)	
C17	0.59074 (47)	0.25739 (56)	−0.25503 (74)	
HO2	0.3393 (41)	0.0944 (44)	−0.3678 (56)	0.0898 (12)
H3A	0.1637 (38)	0.3073 (40)	0.0780 (53)	0.0713 (10)
H3B	0.0947 (32)	0.4053 (38)	0.1749 (45)	0.0580 (8)
H4A	0.1255 (41)	0.2158 (48)	0.3080 (57)	0.0821 (12)
H4B	0.0639 (51)	0.3190 (55)	0.4024 (71)	0.1169 (16)
H6A	0.0480 (37)	0.2853 (38)	−0.1451 (50)	0.0637 (10)
H6B	−0.0046 (26)	0.3756 (32)	−0.0460 (36)	0.0360 (6)
H7A	−0.1706 (36)	0.2220 (36)	−0.1147 (47)	0.0602 (9)
H7B	−0.0917 (32)	0.1559 (39)	−0.2250 (47)	0.0535 (9)
H9A	−0.1966 (30)	0.2014 (32)	0.1715 (41)	0.0466 (7)
H9B	−0.1211 (31)	0.2189 (34)	0.3155 (45)	0.0531 (8)
H10A	−0.0725 (37)	0.4469 (40)	0.3077 (51)	0.0698 (10)
H10B	−0.1884 (39)	0.4033 (42)	0.4050 (57)	0.0836 (11)
H13A	0.5870 (45)	0.3918 (51)	−0.6730 (60)	0.0932 (12)
H13B	0.4616 (60)	0.3172 (62)	−0.7292 (79)	0.1378 (18)
H13C	0.5687 (42)	0.2610 (46)	−0.7923 (61)	0.0808 (12)
H14A	0.5038 (46)	0.3891 (55)	−0.4041 (64)	0.1075 (14)
H14B	0.4063 (40)	0.3009 (41)	−0.4202 (53)	0.0701 (10)
H16A	0.4334	0.3950	−0.1172	0.1773
H16B	0.4049	0.2758	−0.0538	0.1773
H16C	0.3320	0.2925	−0.1639	0.1773
H17A	0.6158 (44)	0.3584 (51)	−0.2275 (61)	0.0915 (12)
H17B	0.6462 (52)	0.2348 (56)	−0.3390 (75)	0.1163 (18)
H17C	0.5879 (43)	0.2184 (51)	−0.1608 (63)	0.0979 (13)

[a] Standard deviations in the least significant digit appear in parentheses in this and subsequent tables.

(i) Atoms Ni2, O1, C12, C13, and C14 lie in a plane with deviations <0.03 Å, while atoms C15 and O2 are each ~0.4 Å out of the plane (Table V).

(ii) The β-carbon atom, C15, and the hydroxyl oxygen atom, O2, are approximately tetrahedral while C12 is essentially trigonal planar (Tables IV and V).

(iii) The Ni2–O2 distance, 1.927 (3) Å, is, as expected, significantly longer than the Ni2–O1 distance, 1.895 (3) Å. The latter compares well with Ni–O distances of 1.881 (5) and 1.896 (5) Å in $Ni[P(C_6H_{11})_3](CH_3)(acac)$[3c] but is longer than the Ni–O distance of 1.836 (5) Å in bis(dipivaloylmethanido)nickel.[3e]

(iv) The C–O distance, 1.268 (5) Å, is in the range observed for various acac complexes, e.g., 1.264 (5),[3d] 1.279 (5),[3a] and 1.314 (10) Å.[3e] The C–$O_{hydroxyl}$ distance, 1.498 (5) Å, is also within the range of published values for transition-metal–alcohol complexes.[9]

Table III. Anisotropic Temperature Factors (Å^2) for [Ni(diacetone alcohol)$_2$][Ni(NCS)$_4$(CEP)$_2$][a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.02900 (34)	0.03799 (37)	0.03246 (35)	0.01121 (26)	−0.00403 (25)	0.00720 (26)
Ni2	0.04812 (43)	0.04325 (41)	0.04161 (40)	0.01299 (32)	−0.00200 (31)	0.01410 (31)
P	0.03658 (37)	0.03649 (38)	0.03467 (37)	0.01061 (28)	−0.00758 (28)	0.00710 (28)
S1	0.0349 (4)	0.0964 (7)	0.0576 (5)	0.0236 (4)	−0.0043 (3)	0.0263 (5)
S2	0.0676 (7)	0.1324 (11)	0.0481 (5)	−0.0119 (7)	−0.0051 (5)	0.0379 (6)
N1	0.0351 (14)	0.0478 (15)	0.0497 (15)	0.0124 (11)	−0.0077 (11)	0.0070 (11)
N2	0.0520 (16)	0.0530 (16)	0.0456 (15)	0.0190 (13)	−0.0020 (13)	0.0145 (12)
N3	0.0658 (22)	0.0783 (24)	0.1004 (30)	0.0181 (19)	−0.0437 (22)	−0.0058 (21)
N4	0.0939 (26)	0.0742 (21)	0.0510 (18)	0.0247 (19)	−0.0131 (17)	0.0273 (16)
N5	0.0741 (24)	0.0854 (26)	0.1000 (29)	0.0273 (20)	−0.0028 (21)	0.0512 (23)
O1	0.0784 (19)	0.0679 (17)	0.0692 (17)	0.0201 (14)	−0.0016 (14)	0.0264 (14)
O2	0.0710 (18)	0.0675 (17)	0.0678 (17)	0.0218 (14)	0.0006 (14)	0.0206 (13)
C1	0.0360 (15)	0.0425 (15)	0.0343 (14)	0.0081 (12)	−0.0072 (11)	0.0086 (12)
C2	0.0436 (16)	0.0498 (17)	0.0412 (17)	0.0107 (13)	−0.0104 (14)	0.0115 (13)
C3	0.0441 (17)	0.0474 (18)	0.0498 (19)	0.0087 (14)	−0.0125 (15)	0.0086 (14)
C4	0.0518 (20)	0.0629 (23)	0.0440 (19)	0.0111 (17)	−0.0151 (15)	0.0033 (16)
C5	0.0575 (21)	0.0610 (22)	0.0546 (20)	0.0238 (18)	−0.0219 (17)	−0.0054 (17)
C6	0.0434 (17)	0.0454 (18)	0.0416 (16)	0.0115 (14)	−0.0051 (13)	0.0152 (14)
C7	0.0560 (20)	0.0471 (19)	0.0425 (17)	0.0111 (15)	−0.0126 (15)	0.0142 (15)
C8	0.0559 (19)	0.0560 (19)	0.0418 (17)	0.0154 (15)	−0.0093 (14)	0.0125 (15)
C9	0.0471 (17)	0.0434 (16)	0.0377 (15)	0.0169 (13)	−0.0047 (13)	0.0062 (13)
C10	0.0589 (21)	0.0523 (20)	0.0533 (20)	0.0262 (17)	−0.0098 (16)	0.0009 (15)
C11	0.0518 (20)	0.0483 (19)	0.0743 (24)	0.0178 (16)	0.0022 (17)	0.0204 (17)
C12	0.0436 (16)	0.0426 (17)	0.0566 (19)	0.0091 (13)	−0.0062 (14)	0.0186 (14)
C13	0.0755 (28)	0.0695 (27)	0.0648 (26)	0.0248 (23)	0.0049 (22)	0.0351 (22)
C14	0.0612 (23)	0.0530 (22)	0.0618 (22)	0.0179 (18)	−0.0096 (18)	0.0172 (17)
C15	0.0711 (23)	0.0486 (18)	0.0470 (18)	0.0203 (17)	−0.0092 (16)	0.0076 (15)
C16	0.1463 (50)	0.0756 (30)	0.0610 (26)	0.0547 (32)	0.0110 (29)	0.0125 (22)
C17	0.0791 (33)	0.0893 (36)	0.0831 (34)	0.0090 (27)	−0.0357 (28)	0.0198 (28)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)]$.

Table IV. Selected Bond Lengths (Å) and Angles (deg)

(A) [Ni(diacetone alcohol)$_2$]$^{2+}$

Ni2-O1	1.895 (3)	C15-C16	1.536 (7)
Ni2-O2	1.927 (3)	C15-C17	1.520 (8)
O1-C12	1.268 (5)	C15-O2	1.498 (5)
C12-C13	1.506 (6)	O2-HO2	1.174 (54)
C12-C14	1.476 (5)	C-H(methyl)	0.996 (25)[a]
C14-C15	1.529 (6)	C-H(methylene)	0.924 (41)[a]
O1-Ni2-O2	90.30 (13)	C14-C15-C17	112.06 (38)
Ni2-O1-C12	132.14 (27)	C14-C15-C16	108.26 (36)
O1-C12-C13	121.64 (35)	C14-C15-O2	108.43 (32)
O1-C12-C14	123.32 (34)	C16-C15-C17	111.78 (41)
C13-C12-C14	114.96 (35)	Ni2-O2-C15	117.45 (24)
C12-C14-C15	118.10 (35)	C15-O2-HO2	108.8 (25)
C17-C15-O2	108.21 (36)	Ni2-O2-HO2	104.0 (25)
C16-C15-O2	107.96 (35)		

(B) [Ni(NCS)$_4$(CEP)$_2$]$^{2-}$

Ni1-N1	2.072 (3)	C5-N3	1.120 (6)
Ni1-N2	2.068 (3)	P-C6	1.832 (4)
Ni1-P	2.420 (1)	C6-C7	1.527 (5)
N1-C1	1.152 (4)	C7-C8	1.463 (5)
C1-S1	1.637 (3)	C8-N4	1.135 (5)
N2-C2	1.144 (4)	P-C9	1.834 (3)
C2-S2	1.632 (3)	C9-C10	1.538 (5)
P-C3	1.833 (4)	C10-C11	1.460 (6)
C3-C4	1.535 (5)	C11-N5	1.132 (6)
C4-C5	1.467 (6)	C-H(methylene)	0.956 (13)[a]
Ni1-N1-C1	160.77 (26)	N1-C1-S1	177.99 (29)
Ni1-N2-C2	163.90 (28)	N2-C2-S2	179.00 (33)
N1-Ni1-N2	87.60 (11)	C4-C5-N3	178.18 (45)
N1-Ni1-P	92.46 (8)	C7-C8-N4	176.96 (41)
N2-Ni1-P	90.21 (8)	C10-C11-N5	178.80 (45)

[a] Weighted average.

Table V. Least-Squares Planes for [Ni(diacetone alcohol)$_2$] [Ni(NCS)$_4$(CEP)$_2$][a]

Plane No. 1,
Equation: $-0.9374X - 0.2819Y - 0.2047Z + 4.6232 = 0$
Atoms in Plane: Ni2, O1, C12, C13, C14

Distances

Ni2	0.023	C13	0.027 (6)	C15	−0.382 (4)
O1	−0.028	C14	0.002 (5)	O2	0.400 (3)
C12	−0.025 (4)				

Plane No. 2, Equation: $0.2042X - 0.9386Y - 0.2783Z = 0$
Atoms in Plane: Ni1, N1, N2

Distances

C2	−0.049 (3)	S2	−0.117 (2)

Plane No. 3, Equation: $0.1142X + 0.3069Y - 0.9449Z = 0$
Atoms in Plane: Ni1, N1, P

Distances

C1	0.126 (3)	S1	0.323 (1)

[a] Orthogonal coordinates X, Y, and Z used in these calculations were obtained from fractional coordinates using the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & 1/c^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

(v) The "bite angle" of this ligand is 90.30 (13)°, somewhat smaller than that observed for nickel β-diketone complexes, e.g., 94.6 (4)[3e] and 92.9 (4)°.[3c] In the same two examples, Ni–O–C angles lie in the range 126–128°. Here, the Ni–$O_{ketonic}$–C angle is somewhat larger, 132.14 (27)°, while the Ni–$O_{hydroxyl}$–C angle is considerably smaller, 117.45 (24)°. An indication of strain in this ring system is also given by the C12–C14–C15 angle of 118.10 (35)°.

[Ni(NCS)$_4$(CEP)$_2$]$^{2-}$. The molecular structure of the anion, showing 50% probability ellipsoids for atoms refined anisotropically, is depicted in Figure 2. The phosphine ligand geometry is normal for CEP complexes.[2,10] The Ni–P (2.420 (1) Å) and Ni–N (2.068 (3), 2.072 (3) Å) distances are similar to those found in octahedral, polymeric NiX_2CEP_2 complexes [X = Cl, Ni–P = 2.438 (1) Å, Ni–N(nitrile) = 2.099 (2) Å; X = Br, Ni–P = 2.445 (1) Å, Ni–N(nitrile) = 2.082 (3) Å].[2,11]

Large deviations from linearity occur in the Ni1–N1–C1 and Ni2–N2–C2 angles, 160.77 (26) and 163.90 (28)°, respectively. Inspection of Table V shows that these deviations occur largely in the Ni1–N1–P and Ni1–N1–N2 planes. This apparently occurs with some distortion of the P–Ni1–N1 and N1–Ni1–N2 angles from 90° (Table IVB). Apart from weak

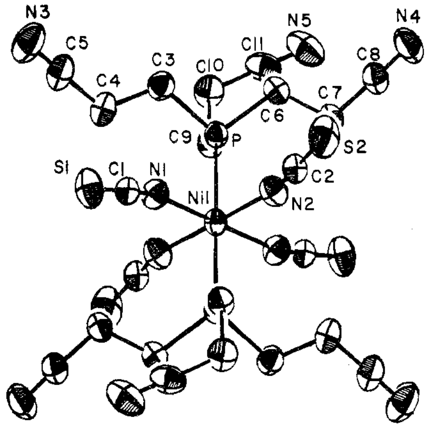

Figure 2. Molecular structure of the $\{Ni[NCS]_4[P(CH_2CH_2CN)_3]_2\}^{2-}$ ion.

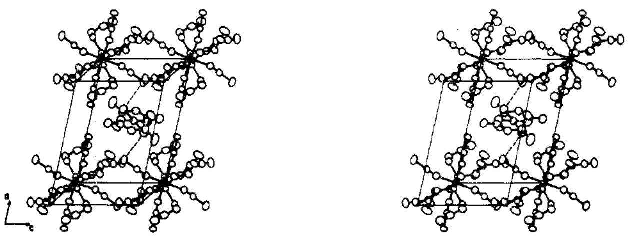

Figure 3. A stereoscopic view of the unit cell contents.

hydrogen bonding to S2 (vide infra), the reason for these distortions is obscure. There are no unusually short inter- or intramolecular contacts to the thiocyanate groups. It appears (Figure 2) that the distortions are consistent with a complex conformation of relatively low energy. It has been demonstrated that large variations in bond angles may arise in closely related conformers of transition-metal complexes.[12] In any event, the M–N–C angles are within the range of reported values (140–180°).[13]

Crystal Structure. The crystal structure (Figure 3) consists of discrete anions and cations, with a weak hydrogen bond (dotted line in Figure 3, S2···HO2–O2). The S–O distance is 3.41 Å and the S2–HO2–O2 angle is 166.6°. There are no other short or significant contacts ≤3.8 Å. It has been demonstrated that $M(NCS)_n$ compounds, where M is a first-row transition metal and $n = 4–6$, are stabilized by large cations of preferably equal but opposite charge.[13] It seems likely here that the anion–cation effect is mutual.

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Registry No. $[Ni(diacetone\ alcohol)_2][Ni(NCS)_4(CEP)_2]$, 68122-36-1; $Ni(NCS)_2$, 13689-92-4; acetone, 67-64-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (Table VI) (12 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, and Texas A&M University, College Station, Texas 77843

Reactions of Metal-to-Metal Multiple Bonds. 5.[1] Addition of Nitric Oxide to Hexa-*tert*-butoxyditungsten. Preparation, Properties, and Structural Characterization of Tri-*tert*-butoxy(nitrosyl)(pyridine)tungsten

M. H. CHISHOLM,*[2a] F. A. COTTON,*[2b] M. W. EXTINE,[2b] and R. L. KELLY[2a]

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The reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and nitric oxide (2 equiv) in hydrocarbon solvents yields an insoluble pale yellow product of empirical formula $W(O\text{-}t\text{-}Bu)_3NO$ ($\nu(NO)$ 1565 cm^{-1}). Addition of the nitrogen donor ligands NH_3, NMe_3, and pyridine causes the above compound to dissolve with the formation of mononuclear compounds $W(O\text{-}t\text{-}Bu)_3(NO)(L)$. The yellow crystalline compound $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ ($\nu(NO)$ 1555 cm^{-1}) has been obtained directly by the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and NO (2 equiv) in pyridine as the solvent. The compound crystallizes in the space group $P2_1/n$ with $Z = 4$ and unit cell dimensions $a = 9.694$ (2) Å, $b = 15.686$ (3) Å, $c = 14.358(2)$ Å, $\beta = 97.40$ (1)°, and $V = 2165.1$ (7) $Å^3$. The coordination geometry of the WO_3N_2 moiety is a slightly distorted trigonal bipyramid with the axial positions occupied by the nitrogen atoms of the nitrosyl and pyridine ligands. The tungsten atom is displaced 0.34 Å toward the nitrosyl ligand from the equatorial plane of the three alkoxy oxygen atoms. There is a linear W–N–O moiety with a short W–N bond distance, 1.732 (8) Å, whereas the W–N bond distance to the coordinated pyridine is long, 2.323 (7) Å.

Introduction

Previously we have shown that the molybdenum-to-molybdenum triple bond in the dinuclear alkoxides $Mo_2(OR)_6$[3] is cleaved as in reaction 1[4] where R = Me_3C, Me_2CH, and Me_3CCH_2.

$$(RO)_3Mo{\equiv}Mo(OR)_3 + 2NO \rightarrow [Mo(OR)_3(NO)]_2 \qquad (1)$$