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Nickel Complexes of Thiohydrazonates. 3.[1,2] Crystal and Molecular Structures of [2,4-Pentanedione bis(thioacethydrazonato)]nickel(II)–Acetonitrile Adduct, Tetrabutylammonium [2,4-Pentanedione bis(thioacethydrazonato)]nickelate(II), and [Pentanetrione 2,4-bis(thioacethydrazonato)]nickel(II)

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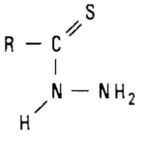
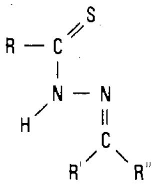
The crystal structures of the three related nickel thiohydrazonate complexes indicated in the title have been studied by single-crystal X-ray crystallography. The parent compound, [2,4-pentanedione bis(thioacethydrazonato)]nickel(II), crystallizes as an acetonitrile adduct, I, in the monoclinic space group $P2_1/c$, with $a = 22.671$ (14) Å, $b = 7.253$ (5) Å, $c = 17.359$ (12) Å, $\beta = 112.90$ (4)°, and $Z = 8$. This compound is an acid and the corresponding base has been crystallized as a tetra-*n*-butylammonium salt. This latter compound, II, crystallizes in the monoclinic space group $P2_1/c$ with $a = 21.662$ (3) Å, $b = 8.7604$ (9) Å, $c = 16.427$ (3) Å, $\beta = 101.49$ (2)°, and $Z = 4$. The complex formed by air oxidation of the acid or the anion is a thiohydrazonate complex, III, derived from 2,3,4-pentanetrione and it crystallizes in the triclinic space group $P\bar{1}$, $a = 7.567$ (3) Å, $b = 9.957$ (4) Å, $c = 10.939$ (5) Å, $\alpha = 123.09$ (2)°, $\beta = 107.47$ (2)°, $\gamma = 91.19$ (3)°, and $Z = 2$. The structures contain planar nickel(II) complexes with similar coordination of the nickel atoms. The acetonitrile molecules in I are disordered. The two crystallographically independent molecules in I have similar molecular dimensions, but they do not have as high a symmetry as the complexes in II and III both of which have an effective twofold axis of symmetry. The bond lengths in the acetylacetone part of the ligand in the structures of I and II are similar, indicating that I is present in a dipolar tautomeric form. This result is supported by ^{1}H NMR measurements. A comparison is given of the molecular dimensions of the structures internally and of related compounds. Finally the observed color differences between the three structures, of which I and II are red and III is green, are discussed in terms of simple MO theory.

Introduction

It has been known that molecules with the general formulas





are able to act as chelate ligands for transition-metal ions since the pioneering work by Jensen.[3,4] Best known are the complexes of thiosemicarbazide and thiosemicarbazones which have attracted interest for a number of reasons. Thus some free ligands and their copper(II) complexes have been found to be biologically active in several ways.[5] Nickel(II) complexes of thiosemicarbazides and thiosemicarbazones are structurally very varied; in addition to planar four-coordinated complexes of both cis and trans sulfur arrangements,[6,7] there are also known complexes with five-[8] and six-coordination.[9,10] Nickel(II) complexes of dithiosemicarbazones of diketones have been found to undergo reversible redox reactions with the normal potentials of one-electron transfer reactions showing a systematic variation with the substituents.[11] In this con-

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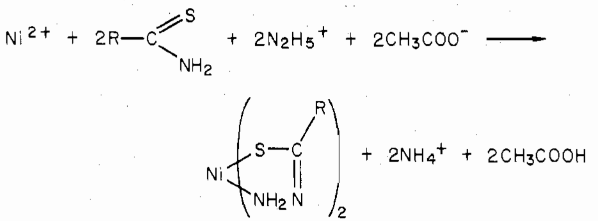
nection it is apparent that complexes of thioacylhydrazonates not having active protons are of special interest, and accordingly Holm and co-workers studied the electrochemistry of complexes of thiobenzhydrazide.[12] Thiobenzhydrazide was first made by Holmberg,[13] and later Jensen[14] demonstrated its similarity to thiosemicarbazide with respect to the complex chemistry. A large selection of N-substituted thiohydrazides was characterized by Jensen and Pedersen[15] while the list of unsubstituted thiohydrazides mainly includes some derived from acids without any α-hydrogen atoms. It has been concluded that aliphatic thiohydrazides containing α hydrogens are unstable because they readily undergo ring-closure reactions, and this may be the reason why the potentially useful ligands have not been prepared. However, recently this difficulty has been overcome by a direct synthesis of thioacylhydrazides according to the reaction[16]


(A)

Ketone thioacylhydrazonato complexes can be obtained from a bis(thioacylhydrazidato)nickel(II) complex by reaction with the ketone in dimethyl sulfoxide or directly from Ni^{2+} with a reaction analogous to A in the presence of the ketone.[1] This remarkable example of the nucleophilicity of hydrazine has been utilized to prepare a series of nickel(II) complexes some of which are close analogues to corresponding thiosemicarbazone complexes as well as some which have no known analogue because the free thiosemicarbazone is unknown.

The thioacethydrazonates dealt with in this paper are expected to be unstable as they are derivatives of acetic acid. Thioacethydrazide has not yet been isolated, but it must possess some stability since the bis(thioacethydrazidato)nickel(II) complex, $[Ni(tah)_2]$, disproportionates with acid:

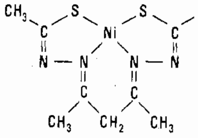
$$3[Ni(tah)_2] + 6H^+ \rightarrow Ni^{2+} + 2[Ni(Htah)_3]^{2+} \quad (B)$$

The complex ion $[Ni(Htah)_3]^{2+}$ can further be used for preparation, e.g., of the corresponding cobalt(III) complex.[17]

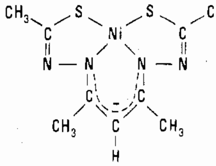
The structure of $[Ni(tah)_2]$ was determined in order to verify that reaction A had indeed taken place.[16] When methyl ketones, e.g., acetone and acetophenone, react with $[Ni(tah)_2]$ or with uncoordinated hydrazide, the reaction could lead to a type of complex analogous to the Curtis condensation product.[18] However, the structure of bis(acetophenone thioacethydrazonato)nickel(II), $[Ni(tah\text{-}acetophenone)_2]$, showed that the complex contains the simple ketone hydrazone.[19] The structure was surprising since it can be considered a distorted planar complex (ca. 20° between the chelate groups) with a cis arrangement around the nickel ion and an unexpected syn configuration of the two phenyl groups.

In complexes derived from a bis(thioacylhydrazone) of a *vic* diketone some delocalization from one thioacylhydrazonato part to the other is possible. This could be the reason for the obvious color difference between the above mentioned acetophenone derivative which is red-brown and of [butanedione bis(thioacethydrazonato)]nickel(II), $[Ni((tah)_2(diacetyl))]$, which is intensely green. However, the bond distances within the tetradentate ligand in [butanedione bis(phenylacet thiohydrazonato)]nickel(II), $[Ni((path)_2(diacetyl))]$, did not show the effect of cross conjugation.[2]

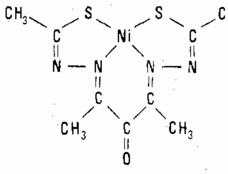
The three structures determined in this work are complexes derived from 2,4-pentanedione (acetylacetone). They seem to be the first dihydrazone derivatives reported for acetylacetone although other diimines of this diketone are known, e.g., the dioxime. The complex [2,4-pentanedione bis(thioacethydrazonato)]nickel(II), I, $[Ni((tah)_2acacH)]$, is an acid, and if the proton is located as indicated by the name of the compound (see structure I), then no cross conjugation is possible.


I.

In the anion studied here as the tetrabutylammonium salt, $(C_4H_9)_4N[Ni((tah)_2acac)]$, II, delocalization over the bridging acetylacetone part is possible.


II.

The two compounds, however, are both orange-red, and they have similar electronic spectra in solution. The compounds can be oxidized by air in a $CaCO_3$-buffered slurry. In this way a very intensely green complex is obtained. An infrared absorption at ca. 1650 cm^{-1} suggests the presence of an oxo group as shown in structure III, $[Ni((tah)_2acacO)]$.[1] The X-ray investigation has proved this structure to be correct.


III

Experimental Section

Crystal Data. The compounds were prepared according to the previously published methods.[1] $[Ni((tah)_2acacH)]$ was obtained as an ethanol adduct and was heated at 100 °C for 3 h under vacuum to remove the ethanol. Crystals suitable for X-ray diffraction work were obtained by Soxhlet extraction with acetonitrile in a nitrogen atmosphere. The chemical analyses indicated that the compound crystallizes with one molecule of the solvent per nickel atom. Anal. Calcd for $C_{11}H_{17}N_5S_2Ni$: C, 38.2; H, 5.01; N, 20.47; S, 18.75. Found: C, 38.87; H, 5.27; N, 20.70; S, 18.08. To prevent oxidation and deterioration of the crystals used in the diffraction work, these were covered with Philips PR 9247/1000 glue. $(C_4H_9)_4N[Ni((tah)_2acac)]$ was recrystallized from acetone and $[Ni((tah)_2acacO)]$ from a 3:1 acetone–water mixture. For each of the compounds a set of oscillation, Weissenberg, and precession photographs was taken. These films were used to obtain information about crystal symmetry and space group and to get preliminary values for the unit cell parameters.

$[Ni((tah)_2acacH)]\cdot CH_3CN$ grows as bright orange-red, platelike crystals which are monoclinic and elongated in the [010] direction. The systematically absent reflections are $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The space group is uniquely determined to be $P2_1/c$.

$(C_4H_9)_4N[Ni((tah)_2acac)]$, II, crystallizes as very thin red plates belonging to the monoclinic crystal system, elongated in the [010] direction. The plate faces are {100}. Other developed faces are {001}, $\{0\bar{1}\bar{1}\}$, and $\{0\overline{11}\}$. The systematically absent reflections as above prove that the space group is $P2_1/c$.

$[Ni((tah)_2acacO)]$, III, crystallizes as very thin green needles with the *a* axis as the needle axis. The diffraction pattern exhibits $\bar{1}$ symmetry indicating that the crystals are triclinic and the possible space groups are $P1$ and $P\bar{1}$. The space group was assumed to be $P\bar{1}$ and this was confirmed by the structure solution.

^{1}H NMR Spectra. [2,4-Pentanedione bis(phenylacet thiohydrazonato)]nickel(II), $[Ni((path)_2acacH)]$, was prepared as described earlier.[1] ^{1}H NMR spectra were recorded on a Bruker HX

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

	[Ni((tah)$_2$acacH)]·CH$_3$CN, $C_{11}H_{17}N_5NiS_2$, I	(C$_4$H$_9$)$_4$N[Ni((tah)$_2$acac)], $C_{25}H_{49}N_5NiS_2$, II	[Ni((tah)$_2$acacO)], $C_9H_{12}N_4ONiS_2$, III
a, Å	22.671 (14)	21.662 (3)[c]	7.567 (3)
b, Å	7.253 (5)	8.7604 (9)	9.757 (4)
c, Å	17.359 (12)	16.427 (3)	10.939 (5)
α, deg	90	90	123.09 (2)
β, deg	112.90 (4)	101.49 (2)	107.47 (2)
γ, deg	90	90	91.19 (3)
V, Å^3	2629	3055	627
d_{calcd} (d_{obsd}), g/cm^3	1.73 (~1.6)[a]	1.19 (1.21)[a]	1.668 (1.674)[a]
Z	8	4	2
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
cryst dimensions, mm	0.10 × 0.15 × 0.25	0.037 × 0.13 × 0.40	0.055 × 0.063 × 0.43
scan rate, deg/min	2	1	1
bkgd counts, s	10	20	20
scan range, deg	$2.4 + 0.692 \tan\theta$	$2.4 + 0.692 \tan\theta$	$3.8 + 0.692 \tan\theta$
2θ limits, deg	2.4–42	2.4–40	2.4–50
octants measured	hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$	hkl, $hk\bar{l}$	hkl, $hk\bar{l}$, $h\bar{k}l$, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}\bar{l}$
linear abs coeff, cm^{-1}	17.8	7.9	18.6
no. of obsd reflections	1529	1741	1608
no. of variables	226	299	202
error in an observation of unit weight[b]	0.92	1.16	2.42
R, %	4.9	5.5	3.7
R_w, %	4.5	4.9	3.9

[a] Measured by flotation in: I, an aqueous solution of KI and HgI$_2$; II, an aqueous solution of KI; III, a mixture of bromobenzene and ethylene bromide. [b] Defined as $\Sigma w(\Delta F)^2/(n - m)$, where n is the number of reflections and m is the number of variables. [c] Cu Kα radiation was used in the determination of unit cell dimensions for II.

90 spectrometer using CDCl$_3$ and (CD$_3$)SO as solvents.

Data Collection and Data Reduction. A Picker FACS-1 four-circle diffractometer was used to collect the diffraction data at 22 °C for the three compounds. Mo Kα radiation monochromatized from a highly mosaic graphite crystal was used. The takeoff angle was 4°. The setting angles for a minimum of 12 reflections were optimized automatically on the diffractometer, and these values were used in a least-squares refinement of the orientation matrix and the unit cell parameters. In all cases diffraction data were obtained by operating the diffractometer in the θ–2θ scan mode using a symmetrical scan range. Background counts were made at each end of the scan range. The intensities of three standard reflections were measured for every 40 reflections during the data collection. These measurements indicated that no deterioration or misalignment of the crystals had occurred during the collection of the three data sets. Table I contains additional information about the data collections. The data sets were processed by a data reduction program of local origin. The integrated intensities were reduced to structure amplitudes $|F_o|$ according to the expressions

$$F_o^2 = (N_T - K(N_{B1} + N_{B2}))/Lp$$

$$\sigma(F_o^2) = (N_T + K^2(N_{B1} + N_{B2}))^{1/2}/Lp$$

where N_T, N_{B1}, and N_{B2} are the total peak count and the two background counts. K is the ratio of the peak scan time to the total background scan time. Lp is the Lorentz–polarization factor. An absorption correction was applied to the data measured for [Ni((tah)$_2$acacO)] by use of a Gaussian numerical integration program. The criterion $I/\sigma(I) > 2.0$ was used to classify reflections as observed in processing of the data sets for [Ni((tah)$_2$acacO)] and (C$_4$H$_9$)$_4$N[Ni((tah)$_2$acac)], whereas for [Ni((tah)$_2$acacH)] the observed reflections were those which had $I/\sigma(I) > 3.0$. In the structure solutions and refinements only the observed reflections were used. In the final data sets symmetry equivalent reflections were averaged.

Structure Solution and Refinement. The three structures were solved by conventional techniques and refined by the method of least squares, minimizing $\sum w(|F_o| - |F_c|)^2$. The unweighted and weighted residuals are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$. The scattering factors used in the calculations were by Cromer and Mann[20] using the values for the uncharged atoms, except for hydrogen where the values by Stewart et al.[21] were used. The anomalous scattering corrections added to the scattering factors for nickel and sulfur were those calculated by Cromer and Liberman.[22] The computer programs employed in this work were the Vanderbilt system[23] (diffractometer operations), MULTAN[24] (structure determination), the X-RAY system[25] (crystal structure analysis), SIMPLEX[26] (weight functions), and ORTEP II[27] (illustrations). A more detailed description of the three structure determinations will be given in the following.

I. [Ni((tah)$_2$acacH)]·CH$_3$CN. The positions for the two nickel atoms and two of the sulfur atoms were determined from the three dimensional Patterson function. The positions for the heavier atoms in the complexes were found in two successive Fourier syntheses. A difference Fourier calculated after a unit-weighted least-squares refinement of the scale factor and positional and isotropic thermal parameters showed only two major peaks. These were interpreted as corresponding to the density of the nitrogen atoms (N(5) and N(5)′) in the two acetonitrile molecules. The parameters for these atoms were included in the following refinements in which anisotropic temperature factors for the nickel and sulfur atoms were introduced. A difference Fourier synthesis calculated after these refinements showed no significant peaks but only diffuse density in the area, where one would expect the carbon atoms of the acetonitrile molecules to be located. Several different attempts were made to describe the scattering from the disordered acetonitrile molecules during the subsequent refinements where anisotropic thermal parameters for the methyl carbon atoms also were included. By use of Hamiltons' R-value test,[28] the best model seems to be the one where two atoms are used for each acetonitrile group, a fully populated nitrogen atom which has anisotropic temperature factors, and a carbon atom with an isotropic temperature factor which has a population parameter of 0.5.

The positions for the hydrogen atoms were found in a difference Fourier synthesis calculated after a unit-weighted refinement of the scale factor and positional and thermal parameters (Ni, S, CH$_3$, N(5), and N(5)′ anisotropic) with $R = 0.077$. All the hydrogen atoms of the methyl groups except for CH$_3$CN could be located, but only one peak was found close to the methylene group in the acetylacetone part of the ligand. The thermal parameters for the hydrogen atoms were chosen to have the value of the refined isotropic temperature factor of the atom to which they are bonded. Including but not refining the parameters for the hydrogen atoms in the refinement reduced the R value to 0.068. During the final cycles of weighted least-squares refinements, the positional parameters for the hydrogen were fixed to idealized positions (C–H = 1.02 Å). The weights used were of the form $w = (6.67 + 0.08\sigma^2(F) - 0.14F + 0.0009F^2)^{-1}$. In the final cycle of least-squares refinement the maximum shift of the parameters was 0.19σ, $R = 0.049$, and $R_w = 0.045$.

A final difference Fourier map showed no significant features. The largest peaks which have heights around 0.4 e/Å^3 were not found in

Table II. Positional and Thermal Parameters[30] for [Ni((tah)$_2$acacH)]·CH$_3$CN[a]

	molecule 1				molecule 2			
atom	x	y	z	U^b	x	y	z	U^a
Ni	0.10360 (7)	0.2434 (2)	0.02028 (7)	0.035	0.60072 (6)	0.2111 (2)	0.05549 (7)	0.034
S(1)	0.1771 (1)	0.1768 (5)	0.1372 (2)	0.053	0.6716 (2)	0.1756 (4)	0.0053 (2)	0.055
S(2)	0.0360 (1)	0.2144 (5)	0.0769 (2)	0.049	0.5313 (1)	0.2320 (5)	−0.0688 (2)	0.052
N(1)	0.2322 (4)	0.2497 (12)	0.0324 (5)	0.042 (2)	0.7306 (4)	0.1844 (12)	0.1698 (5)	0.044 (2)
N(2)	0.1674 (4)	0.2737 (11)	−0.0218 (4)	0.034 (2)	0.6660 (4)	0.1977 (11)	0.1608 (5)	0.035 (2)
N(3)	0.0359 (4)	0.2915 (11)	−0.0804 (4)	0.035 (2)	0.5363 (3)	0.2375 (11)	0.0939 (4)	0.031 (2)
N(4)	−0.0258 (4)	0.2916 (11)	−0.0797 (4)	0.036 (2)	0.4739 (4)	0.2611 (11)	0.0336 (4)	0.037 (2)
C(1)	0.3070 (6)	0.1724 (16)	0.1698 (6)	0.057	0.8024 (6)	0.1696 (18)	0.0975 (8)	0.066
C(2)	0.2400 (5)	0.2086 (14)	0.1072 (6)	0.039 (3)	0.7368 (5)	0.1761 (14)	0.1001 (6)	0.042 (3)
C(3)	0.1573 (5)	0.3115 (13)	−0.1000 (6)	0.031 (2)	0.6589 (5)	0.1984 (14)	0.2333 (6)	0.037 (3)
C(4)	0.2132 (5)	0.3241 (16)	−0.1263 (6)	0.050	0.7154 (5)	0.1797 (17)	0.3130 (6)	0.054
C(5)	0.0971 (5)	0.3350 (14)	−0.1618 (6)	0.039 (3)	0.5986 (5)	0.2116 (14)	0.2364 (5)	0.034 (2)
C(6)	0.0387 (5)	0.3272 (14)	−0.1552 (6)	0.037 (3)	0.5388 (5)	0.2291 (14)	0.1728 (5)	0.035 (2)
C(7)	−0.0214 (5)	0.3556 (18)	−0.2311 (6)	0.055	0.4817 (5)	0.2379 (20)	0.1918 (6)	0.058
C(8)	−0.0311 (5)	0.2601 (17)	−0.0085 (6)	0.051 (3)	0.4673 (5)	0.2614 (15)	−0.0459 (6)	0.044 (3)
C(9)	−0.0950 (5)	0.2569 (17)	−0.0029 (7)	0.057	0.4007 (6)	0.2826 (18)	−0.1123 (6)	0.066
N(5)	0.358 (1)	0.373 (4)	0.034 (2)	0.077	0.8537 (2)	0.086 (1)	0.3025 (7)	0.070
C(10)[c]	0.352 (4)	0.384 (10)	0.052 (5)	0.069 (19)	0.851 (2)	0.286 (5)	0.296 (2)	0.105 (10)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			Molecule 1			
Ni	0.0292 (8)	0.0444 (8)	0.0325 (7)	−0.0021 (8)	0.0125 (6)	−0.0016 (7)
S(1)	0.041 (2)	0.080 (2)	0.034 (2)	0.000 (2)	0.010 (1)	0.006 (2)
S(2)	0.045 (2)	0.063 (2)	0.049 (2)	−0.005 (2)	0.028 (2)	−0.002 (2)
C(1)	0.038 (8)	0.080 (9)	0.039 (7)	−0.007 (7)	−0.001 (6)	−0.002 (6)
C(4)	0.036 (8)	0.076 (9)	0.042 (6)	0.000 (6)	0.002 (6)	0.009 (6)
C(7)	0.029 (7)	0.093 (10)	0.033 (6)	0.019 (7)	0.002 (5)	0.002 (6)
C(9)	0.041 (7)	0.061 (8)	0.085 (8)	−0.007 (7)	0.040 (7)	−0.011 (8)
N(5)	0.032 (10)	0.121 (15)	0.079 (17)	0.003 (8)	0.023 (10)	0.015 (11)
			Molecule 2			
Ni′	0.0308 (8)	0.0412 (8)	0.0306 (7)	−0.0019 (7)	0.0127 (6)	−0.0003 (7)
S(1)′	0.059 (2)	0.071 (2)	0.044 (2)	0.003 (2)	0.030 (2)	0.002 (2)
S(2)′	0.054 (2)	0.072 (2)	0.030 (1)	−0.001 (2)	0.015 (1)	0.000 (2)
C(1)′	0.036 (8)	0.090 (10)	0.088 (9)	−0.001 (7)	0.044 (7)	−0.002 (8)
C(4)′	0.039 (8)	0.079 (9)	0.043 (7)	−0.007 (6)	0.015 (6)	−0.002 (6)
C(7)′	0.029 (7)	0.109 (10)	0.037 (6)	−0.007 (8)	0.012 (5)	−0.015 (8)

[a] The atoms from molecule 2 in the structure are marked with a prime when a distinction is necessary. [b] The U's are in Å^2; the isotropic temperature factor is $\exp[-2\pi^2 U(\sin^2\theta)/\lambda^2]$. For the anisotropically refined atoms the equivalent isotropic temperature factor is given as $U = {}^1/_3 \Sigma_i \Sigma_j (U_{ij} a_i^* a_j^*) \bar{a}_i \bar{a}_j$. [c] C(10) has the population parameter 0.5.

the vicinity of the disordered acetonitrile groups.

II. (C$_4$H$_9$)N[Ni((tah)$_2$acac)]. This structure was solved by direct methods using the program system MULTAN.[24] Trial positions for all atoms in the complex ion except the methyl carbon atoms and ten atoms in the tetra-*n*-butylammonium ion were found in an E map based on 450 reflections. The remaining nonhydrogen atoms in the structure were located in a difference Fourier synthesis. A unit-weighted refinement of the scale factor and the positional and thermal parameters (Ni and S anisotropic) converged at $R = 0.101$. A difference Fourier synthesis calculated at this stage of the refinement showed peaks at the expected positions for the hydrogen atoms in the structure. The contribution from the hydrogen atoms was included in the refinement with fixed parameters. The refined isotropic temperature factor for the atom to which the hydrogens are bonded was used as their temperature factor. By inclusion of the contribution from the hydrogen atoms in the refinement, the R value dropped to 0.078. A type of constrained refinement was used to refine the parameters of the tetra-*n*-butylammonium ion. The heavier atoms were refined while the hydrogen parameters were fixed. After convergence, new positional parameters for the hydrogen atoms were calculated in idealized positions (C–H = 1.02 Å), and these new hydrogen parameters were used in the next refinement cycles. By use of Hamiltons' R-value test,[28] anisotropic temperature factors were gradually introduced for all the heavier atoms. The weights used in the refinements followed the expression $w = (2.8 + 2.1\sigma(F)^2 - (0.015F + 0.0003F^2)^{-1}$. After the last cycle of least-squares refinement, the maximum shift of parameters was 0.22σ, $R = 0.055$, and $R_w = 0.049$.

III. [Ni((tah)$_2$acacO)]. Trial positional parameters for the nickel and sulfur atoms in the structure were deduced from the three dimensional Patterson function. The positions for the other nonhydrogen atoms in the structure were determined from two subsequent Fourier maps. After a unit-weighted refinement of the scale factor and positional and anisotropic thermal parameters was performed, the R value was 0.058. A difference map calculated at this stage of the refinement revealed all the hydrogen atoms in the structure. The positional and isotropic thermal parameters for the hydrogen atoms were included in the final cycles of weighted least-squares refinement. The weights followed the expression $w = (2.6 + 1.54\sigma(F)^2 - 0.046F + 0.00142F^2 - 4.06\sin(\theta/\lambda)^{-1}$. The final residuals are $R = 0.037$ and $R_w = 0.039$, and in the last cycle of refinement the maximum shift of parameters is 0.22σ.

Results and Description of the Structures

The positional and thermal parameters for the heavier atoms in the structures are listed in Tables II–IV. The calculated parameters for the hydrogen atoms in [Ni((tah)$_2$acacH)]·CH$_3$CN and (C$_4$H$_9$)$_4$N[Ni((tah)$_2$acac)] and the refined parameters for the hydrogen atoms of [Ni((tah)$_2$acacO)] are given in Tables A1–A3.[30] Listings of observed and calculated structure amplitudes are available.[30]

[Ni((tah)$_2$acacH)]·CH$_3$CN. The stereopair shown in Figure 1a illustrates the packing of this compound. The two crystallographically independent planar molecules in the crystal pack with their coordination plane almost in the glide plane of the crystal forming angles to the twofold axis of 77 and 84°, respectively. This pseudosymmetrical arrangement of the two molecules is also apparent from an inspection of the atomic coordinates listed in Table II, which reveal that the x coordinates of corresponding atoms in the two molecules are related by a translational near-symmetry of $a/2$. A comparison of similar bond lengths and bond angles listed in Table V for the two molecules shows that there are no significant differences

Table III. Positional and Thermal Parameters[29] for $(C_4H_9)_4N[Ni((tah)_2acac)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
				Anion					
Ni	0.76011 (6)	0.84096 (13)	0.50214 (7)	0.0916 (6)	0.0521 (6)	0.0663 (7)	0.0202 (8)	0.0281 (7)	0.0152 (7)
S(1)	0.6808 (1)	0.8738 (3)	0.5595 (2)	0.109 (2)	0.079 (2)	0.074 (2)	0.013 (2)	0.037 (2)	0.001 (2)
S(2)	0.8188 (1)	0.9602 (3)	0.6035 (2)	0.110 (2)	0.066 (2)	0.089 (2)	0.019 (2)	0.022 (2)	0.003 (2)
N(1)	0.6407 (4)	0.7286 (9)	0.4171 (5)	0.087 (7)	0.091 (6)	0.077 (6)	0.026 (5)	0.026 (5)	0.007 (5)
N(2)	0.7053 (4)	0.7418 (8)	0.4168 (5)	0.089 (7)	0.069 (5)	0.058 (5)	0.024 (5)	0.029 (5)	0.016 (4)
N(3)	0.8317 (4)	0.8151 (9)	0.4585 (6)	0.105 (7)	0.048 (5)	0.081 (6)	0.023 (5)	0.035 (6)	0.015 (5)
N(4)	0.8901 (5)	0.8734 (11)	0.4985 (7)	0.092 (8)	0.077 (7)	0.114 (8)	0.010 (6)	0.029 (7)	0.018 (6)
C(1)	0.5581 (5)	0.7845 (14)	0.4904 (7)	0.108 (9)	0.134 (11)	0.123 (9)	0.010 (8)	0.042 (8)	−0.007 (8)
C(2)	0.6261 (5)	0.7893 (11)	0.4820 (6)	0.100 (9)	0.088 (8)	0.077 (7)	0.027 (7)	0.043 (7)	0.010 (6)
C(3)	0.7212 (6)	0.6775 (11)	0.3512 (6)	0.110 (10)	0.052 (6)	0.060 (7)	0.009 (7)	0.029 (7)	0.021 (6)
C(4)	0.6710 (6)	0.5964 (11)	0.2867 (6)	0.152 (10)	0.064 (7)	0.087 (7)	0.021 (7)	0.054 (8)	0.013 (6)
C(5)	0.7821 (7)	0.6757 (12)	0.3370 (6)	0.122 (10)	0.058 (7)	0.081 (8)	0.015 (8)	0.056 (8)	0.016 (6)
C(6)	0.8345 (6)	0.7431 (13)	0.3876 (9)	0.094 (10)	0.059 (7)	0.106 (10)	0.028 (7)	0.051 (9)	0.024 (7)
C(7)	0.8969 (6)	0.7289 (12)	0.3602 (7)	0.144 (10)	0.084 (8)	0.131 (9)	0.031 (7)	0.069 (8)	0.009 (7)
C(8)	0.8873 (6)	0.9437 (12)	0.5672 (8)	0.109 (10)	0.058 (7)	0.111 (10)	0.016 (7)	0.021 (9)	0.019 (7)
C(9)	0.9481 (6)	1.0087 (13)	0.6170 (9)	0.115 (10)	0.087 (9)	0.191 (13)	0.002 (8)	0.016 (9)	0.008 (9)
				Cation					
N(5)	0.7373 (3)	0.0977 (7)	0.1857 (4)	0.0075 (5)	0.032 (4)	0.069 (5)	−0.003 (4)	0.026 (4)	−0.002 (4)
C(11)	0.7880 (4)	−0.0114 (9)	0.1717 (5)	0.088 (7)	0.048 (6)	0.079 (6)	0.018 (6)	0.022 (6)	−0.007 (5)
C(12)	0.8474 (5)	0.0636 (11)	0.1538 (6)	0.079 (7)	0.071 (7)	0.110 (8)	0.002 (6)	0.037 (6)	0.004 (6)
C(13)	0.8921 (5)	−0.0510 (13)	0.1356 (7)	0.093 (9)	0.102 (9)	0.166 (11)	−0.008 (8)	0.070 (8)	−0.017 (8)
C(14)	0.9528 (5)	0.0022 (15)	0.1232 (8)	0.096 (9)	0.143 (11)	0.163 (11)	0.009 (8)	0.048 (8)	−0.011 (9)
C(21)	0.6848 (4)	0.0022 (10)	0.2075 (5)	0.071 (7)	0.059 (6)	0.084 (6)	−0.006 (5)	0.020 (5)	0.001 (5)
C(22)	0.6253 (5)	0.0847 (11)	0.2183 (6)	0.088 (8)	0.071 (7)	0.099 (7)	0.003 (6)	0.029 (6)	0.008 (6)
C(23)	0.5764 (5)	−0.0215 (12)	0.2366 (6)	0.090 (8)	0.091 (8)	0.132 (9)	0.013 (7)	0.050 (7)	0.027 (7)
C(24)	0.5165 (5)	0.0515 (15)	0.2437 (7)	0.096 (10)	0.149 (11)	0.154 (10)	0.014 (9)	0.043 (8)	0.029 (9)
C(31)	0.7622 (4)	0.2090 (8)	0.2562 (5)	0.071 (6)	0.040 (6)	0.078 (6)	0.005 (5)	0.020 (5)	−0.008 (5)
C(32)	0.7867 (4)	0.1376 (11)	0.3405 (6)	0.101 (8)	0.065 (7)	0.074 (6)	0.017 (6)	0.018 (6)	0.006 (6)
C(33)	0.8224 (6)	0.2534 (12)	0.4017 (6)	0.124 (10)	0.077 (8)	0.080 (7)	0.002 (7)	0.000 (7)	0.001 (6)
C(34)	0.8862 (6)	0.2901 (14)	0.3889 (7)	0.124 (11)	0.131 (11)	0.141 (10)	−0.029 (9)	0.008 (9)	−0.020 (9)
C(41)	0.7140 (4)	0.1958 (9)	0.1096 (5)	0.090 (7)	0.048 (6)	0.060 (6)	−0.008 (5)	0.018 (5)	−0.001 (5)
C(42)	0.6913 (5)	0.1081 (11)	0.0306 (6)	0.120 (9)	0.071 (7)	0.084 (7)	−0.004 (6)	0.016 (7)	−0.005 (6)
C(43)	0.6576 (6)	0.2134 (14)	−0.0388 (6)	0.140 (11)	0.112 (10)	0.082 (8)	−0.000 (9)	0.015 (8)	−0.013 (7)
C(44)	0.5942 (7)	0.2451 (18)	−0.0322 (8)	0.123 (11)	0.205 (16)	0.146 (12)	0.022 (11)	0.010 (10)	0.025 (11)

Table IV. Positional and Thermal Parameters[29] for $[Ni((tah)_2acacO)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.23507 (10)	0.10927 (7)	0.05903 (8)	0.0379 (3)	0.0269 (3)	0.0376 (3)	0.0092 (2)	0.0163 (2)	0.0158 (2)
S(1)	0.2877 (2)	0.2902 (1)	0.3029 (2)	0.0662 (9)	0.0358 (6)	0.0434 (7)	0.0184 (6)	0.0234 (6)	0.0159 (5)
S(2)	0.1378 (2)	0.2916 (1)	0.0194 (2)	0.0635 (9)	0.0355 (6)	0.0567 (7)	0.0191 (5)	0.0268 (7)	0.0271 (5)
O(1)	0.2507 (7)	−0.4260 (4)	−0.2407 (4)	0.103 (3)	0.029 (2)	0.052 (2)	0.016 (2)	0.027 (2)	0.016 (2)
N(1)	0.3834 (7)	0.0130 (5)	0.2682 (5)	0.057 (3)	0.044 (2)	0.040 (2)	0.017 (2)	0.022 (2)	0.022 (2)
N(2)	0.3271 (6)	−0.0386 (5)	0.1116 (5)	0.041 (2)	0.031 (2)	0.041 (2)	0.008 (2)	0.015 (2)	0.018 (2)
N(3)	0.1862 (6)	−0.0370 (5)	−0.1592 (5)	0.043 (2)	0.032 (2)	0.040 (2)	0.007 (2)	0.016 (2)	0.017 (2)
N(4)	0.1147 (7)	0.0171 (5)	−0.2559 (5)	0.055 (3)	0.043 (2)	0.045 (2)	0.014 (2)	0.017 (2)	0.028 (2)
C(1)	0.4186 (13)	0.2313 (9)	0.5321 (7)	0.104 (6)	0.065 (4)	0.047 (3)	0.038 (4)	0.036 (4)	0.028 (3)
C(2)	0.3662 (8)	0.1641 (6)	0.3618 (6)	0.046 (3)	0.046 (3)	0.039 (3)	0.011 (2)	0.015 (2)	0.020 (2)
C(3)	0.3365 (7)	−0.1943 (5)	0.0150 (6)	0.038 (2)	0.033 (2)	0.046 (2)	0.009 (2)	0.017 (2)	0.021 (2)
C(4)	0.4066 (10)	−0.3007 (7)	0.0687 (7)	0.073 (4)	0.042 (2)	0.061 (3)	0.025 (3)	0.034 (3)	0.032 (3)
C(5)	0.2678 (7)	−0.2748 (5)	−0.1563 (5)	0.043 (3)	0.029 (2)	0.042 (2)	0.014 (2)	0.021 (2)	0.015 (2)
C(6)	0.2112 (7)	−0.1892 (5)	−0.2368 (5)	0.038 (2)	0.033 (2)	0.036 (2)	0.006 (2)	0.013 (2)	0.015 (2)
C(7)	0.1689 (10)	−0.2929 (7)	−0.4105 (6)	0.063 (4)	0.038 (2)	0.042 (3)	0.012 (2)	0.018 (3)	0.015 (2)
C(8)	0.0871 (8)	0.1679 (6)	−0.1799 (6)	0.056 (3)	0.044 (2)	0.054 (3)	0.011 (2)	0.020 (2)	0.033 (2)
C(9)	0.0026 (14)	0.2342 (10)	−0.2743 (10)	0.107 (6)	0.066 (4)	0.077 (5)	0.036 (4)	0.043 (5)	0.055 (4)

between the two molecules. The averaged molecular dimensions are shown in Figure 2 which also illustrates the atomic labeling.

The disordered acetonitrile molecules in this structure are situated in channels between the complexes parallel to the twofold axis of symmetry. The distances between the two atoms used to describe the scattering from the acetonitrile are too short and for one group even physically unrealistic, N(5)′–C(10)′ = 0.4 Å. To differentiate between the two types of complexes and solvent molecules in the structure the atoms in molecule 2 are marked with a prime.

$(C_4H_9)_4N[Ni((tah)_2acac)]$. The packing arrangement of this compound illustrated in Figure 1b is determined by van der Waals interactions mainly between the two ions. The shortest contact distance observed in the structure is 3.52 Å between the methyl carbon atom C(1) and the methylene carbon C(13). The anion is planar forming an angle of 30° with the *ac* plane. Bond lengths and bond angles for this ion are reproduced in Table VI. In Table VII are given the bond lengths and the bond and torsion angles for the tetrabutylammonium ion. Two of the *n*-butyl chains have anti conformations, and the remaining two have a 2,3-gauche conformation. The most frequently found conformation of the tetrabutylammonium ion is the energetically favored all-anti,[31] and in structures which contain both anti and gauche *n*-butyl chains, the latter exhibit either disorder or have large thermal ellipsoids.[32] A difference Fourier synthesis calculated for this compound does not contain any residual peaks, and although the thermal parameters are large for the terminal carbon atoms, they are of similar magnitude for the anti and gauche butyl chains thus being an example of an ordered tetrabutylammonium ion containing gauche chains. The idealized symmetry of the

Table V. Bond Lengths (Å) and Bond Angles (deg) in $[\mathrm{Ni}((\mathrm{tah})_2\mathrm{acacH})]\cdot\mathrm{CH_3CN}$

length	molecule 1	molecule 2	length	molecule 1	molecule 2
Ni-S(1)	2.120 (3)	2.119 (4)	C(3)-C(5)	1.379 (12)	1.393 (16)
Ni-S(2)	2.130 (4)	2.123 (3)	C(5)-C(6)	1.373 (18)	1.381 (12)
Ni-N(2)	1.869 (9)	1.854 (7)	C(6)-C(7)	1.495 (12)	1.457 (17)
Ni-N(3)	1.856 (7)	1.836 (9)	C(6)-N(3)	1.350 (14)	1.351 (13)
S(1)-C(2)	1.713 (13)	1.731 (9)	N(3)-N(4)	1.403 (13)	1.405 (9)
C(1)-C(2)	1.507 (14)	1.507 (19)	N(4)-C(8)	1.307 (15)	1.329 (13)
C(2)-N(1)	1.275 (13)	1.271 (15)	C(8)-C(9)	1.491 (19)	1.509 (14)
N(1)-N(2)	1.413 (10)	1.416 (13)	C(8)-S(2)	1.692 (9)	1.661 (13)
N(2)-C(3)	1.315 (12)	1.327 (14)	N(5)-C(10)	1.45 (4)	
C(3)-C(4)	1.507 (18)	1.480 (12)	N′(5)-C′(10)	0.40 (11)	

angle	molecule 1	molecule 2	angle	molecule 1	molecule 2
S(2)-Ni-S(1)	88.58 (13)	88.39 (14)	C(4)-C(3)-C(5)	116.8 (9)	118.2 (10)
N(2)-Ni-S(1)	87.8 (2)	87.6 (3)	C(3)-C(5)-C(6)	128.7 (10)	130.4 (10)
N(3)-Ni-S(2)	88.4 (3)	88.9 (2)	C(7)-C(6)-C(5)	119.9 (10)	120.4 (9)
N(3)-Ni-N(2)	95.3 (4)	95.2 (4)	N(3)-C(6)-C(7)	120.4 (10)	122.5 (7)
Ni-S(1)-C(2)	96.7 (3)	96.5 (5)	N(3)-C(6)-C(5)	119.7 (8)	117.1 (10)
S(1)-C(2)-C(1)	118.8 (8)	117.4 (9)	N(4)-N(3)-C(6)	115.4 (7)	113.2 (8)
C(1)-C(2)-N(1)	118.5 (11)	120.3 (9)	Ni-N(3)-C(6)	127.6 (7)	129.6 (6)
S(1)-C(2)-N(1)	122.6 (7)	122.3 (9)	Ni-N(3)-N(4)	117.0 (6)	117.1 (6)
C(2)-N(1)-N(2)	113.7 (9)	113.0 (8)	C(8)-N(4)-N(3)	117.8 (7)	116.6 (9)
Ni-N(2)-N(1)	119.2 (6)	120.5 (7)	S(2)-C(8)-N(4)	118.8 (9)	119.5 (7)
Ni-N(2)-C(3)	125.3 (6)	126.2 (7)	C(9)-C(8)-N(4)	120.9 (9)	117.9 (10)
N(1)-N(2)-C(3)	115.5 (9)	113.4 (7)	S(2)-C(8)-C(9)	120.3 (9)	122.6 (9)
N(2)-C(3)-C(5)	123.4 (11)	121.3 (8)	Ni-S(2)-C(8)	98.0 (5)	97.9 (3)
N(2)-C(3)-C(4)	119.8 (8)	120.4 (10)			

Table VI. Bond Lengths (Å) and Bond Angles (deg) for the Anion in $(\mathrm{C_4H_9})_4\mathrm{N}[\mathrm{Ni}((\mathrm{tah})_2\mathrm{acac})]$

Lengths

Ni-S(1)	2.138 (4)	Ni-S(2)	2.153 (5)
Ni-N(2)	1.861 (8)	Ni-N(3)	1.849 (11)
S(1)-C(2)	1.723 (11)	S(2)-C(8)	1.712 (14)
C(1)-C(2)	1.508 (16)	C(9)-C(8)	1.515 (17)
C(2)-N(1)	1.286 (14)	C(8)-N(4)	1.297 (17)
N(1)-N(2)	1.405 (13)	N(3)-N(4)	1.399 (13)
N(2)-C(3)	1.321 (14)	N(3)-C(6)	1.336 (17)
C(3)-C(4)	1.532 (15)	C(6)-C(7)	1.514 (19)
C(3)-C(5)	1.386 (21)	C(6)-C(5)	1.396 (17)

Angles

S(2)-Ni-S(1)	89.8 (1)	N(3)-Ni-N(2)	96.3 (4)
N(2)-Ni-S(1)	86.9 (3)	N(3)-Ni-S(2)	87.0 (3)
Ni-S(1)-C(2)	96.4 (4)	Ni-S(2)-C(8)	96.3 (4)
S(1)-C(2)-C(1)	119.0 (8)	S(2)-C(8)-C(9)	120.0 (10)
C(1)-C(2)-N(1)	118.1 (9)	C(9)-C(8)-N(4)	117.5 (12)
S(1)-C(2)-N(1)	123.0 (8)	S(2)-C(8)-N(4)	122.5 (9)
C(2)-N(1)-N(2)	112.2 (8)	C(8)-N(4)-N(3)	112.8 (10)
Ni-N(2)-N(1)	121.5 (6)	Ni-N(3)-N(4)	121.5 (8)
Ni-N(2)-C(3)	125.6 (8)	Ni-N(3)-C(6)	125.6 (8)
N(1)-N(2)-C(3)	112.9 (8)	N(4)-N(3)-C(6)	112.8 (10)
N(2)-C(3)-C(5)	123.7 (9)	N(3)-C(6)-C(5)	123.1 (12)
N(2)-C(3)-C(4)	119.8 (10)	N(3)-C(6)-C(7)	119.8 (10)
C(4)-C(3)-C(5)	116.5 (10)	C(7)-C(6)-C(5)	117.1 (11)
C(3)-C(5)-C(6)	125.6 (11)		

Table VII. Bond Lengths (Å) and Bond and Torsion Angles (deg) for the Tetra-*n*-butylammonium Cation[a]

Lengths

N(5)-C(11)	1.508 (11)	C(22)-C(23)	1.484 (15)
N(5)-C(21)	1.512 (11)	C(23)-C(24)	1.472 (16)
N(5)-C(31)	1.527 (10)	C(31)-C(32)	1.514 (12)
N(5)-C(41)	1.517 (10)	C(32)-C(33)	1.524 (13)
C(11)-C(12)	1.524 (14)	C(33)-C(34)	1.476 (18)
C(12)-C(13)	1.465 (15)	C(41)-C(42)	1.503 (12)
C(13)-C(14)	1.449 (17)	C(42)-C(43)	1.533 (15)
C(21)-C(22)	1.518 (14)	C(43)-C(44)	1.425 (20)

Bond Angles

C(11)-N(5)-C(21)	107.0 (6)	N(5)-C(21)-C(22)	117.5 (7)
C(11)-N(5)-C(31)	111.2 (6)	C(21)-C(22)-C(23)	112.5 (8)
C(11)-N(5)-C(41)	111.4 (6)	C(22)-C(23)-C(24)	114.8 (9)
C(21)-N(5)-C(31)	109.9 (6)	N(5)-C(31)-C(32)	115.8 (6)
C(21)-N(5)-C(41)	111.5 (6)	C(31)-C(32)-C(33)	111.5 (7)
C(31)-N(5)-C(41)	105.8 (5)	C(32)-C(33)-C(34)	114.6 (9)
N(5)-C(11)-C(12)	115.2 (7)	N(5)-C(41)-C(42)	114.7 (6)
C(11)-C(12)-C(13)	111.2 (8)	C(41)-C(42)-C(43)	111.0 (8)
C(12)-C(13)-C(14)	117.7 (10)	C(42)-C(43)-C(44)	112.6 (11)

Torsion Angles

N(5)-C(11)-C(12)-C(13)	−176.2 (7)	C(11)-N(5)-C(21)-C(22)	−175.5 (7)
C(11)-C(12)-C(13)-C(14)	−175.6 (9)	C(21)-N(5)-C(11)-C(12)	−176.5 (7)
N(5)-C(21)-C(22)-C(23)	177.9 (7)	C(31)-N(5)-C(41)-C(42)	175.9 (7)
C(21)-C(22)-C(23)-C(24)	−177.3 (8)	C(41)-N(5)-C(31)-C(32)	178.4 (7)
N(5)-C(31)-C(32)-C(33)	168.4 (8)	C(11)-N(5)-C(31)-C(32)	−60.5 (9)
C(31)-C(32)-C(33)-C(34)	−76.0 (11)	C(11)-N(5)-C(41)-C(42)	54.9 (9)
N(5)-C(41)-C(42)-C(43)	169.4 (8)	C(21)-N(5)-C(31)-C(32)	57.8 (9)
C(41)-C(42)-C(43)-C(44)	−80.0 (12)	C(21)-N(5)-C(41)-C(42)	−64.6 (9)

[a] The first number in the labeling of carbon atoms distinguishes between the different *n*-butyl chains.

cation is C_{2v} which can be seen from Figure 3. The ions are arranged in the crystal with their pseudo-two-fold axis virtually parallel to the crystallographical twofold axis. A drawing of the anion is shown in Figure 4.

$[\mathrm{Ni}((\mathrm{tah})_2\mathrm{acacO})]$. The stereopair in Figure 1c demonstrates the packing in this structure. There are short contacts between adjacent molecules in the direction of the *a* axis: Ni-Ni′, 3.64 Å; C(4)-S(2)′, 3.54 Å; N(2)-S(2)′, 3.64 Å; S(1)-N(3)′, 3.66 Å; C(6)-S(1)′, 3.62 Å). These intermolecular distances are significantly longer than the similar distances found in bis(dimethylglyoximato)nickel(II),[33] and they do not necessarily reflect the presence of a Ni–Ni bond. However, the short intermolecular distances combined with the orientation of the molecules strongly indicate that dipole–dipole attractions are of importance for the packing. Bond lengths and bond angles can be found in Table VIII. The skeleton of the chelate is nearly planar except for the oxygen atom which is displaced sufficiently from the mean plane (Table IX) to make it visible on the ORTEP drawing shown in Figure 5.

Discussion

Comparison of the Three Structures. It is apparent from the bond lengths and bond angles shown in Tables V–VIII that the complexes II and III possess an effective twofold axis of

Table VIII. Bond Lengths (Å) and Bond Angles (deg) for [Ni((tah)$_2$acacO)]

Ni-S(1)	2.141 (2)	Ni-S(2)	2.145 (2)
Ni-N(2)	1.898 (6)	Ni-N(3)	1.897 (5)
S(1)-C(2)	1.717 (7)	S(2)-C(8)	1.721 (6)
C(1)-C(2)	1.507 (10)	C(9)-C(8)	1.497 (15)
C(2)-N(1)	1.296 (6)	C(8)-N(4)	1.296 (7)
N(1)-N(2)	1.408 (7)	N(3)-N(4)	1.403 (8)
N(2)-C(3)	1.313 (6)	N(3)-C(6)	1.302 (6)
C(3)-C(4)	1.486 (11)	C(6)-C(7)	1.503 (8)
C(3)-C(5)	1.479 (8)	C(6)-C(5)	1.499 (9)
C(5)-O	1.216 (5)		
S(2)-Ni-S(1)	87.88 (7)	N(3)-Ni-N(2)	98.9 (2)
N(2)-Ni-S(1)	87.6 (1)	N(3)-Ni-S(2)	87.7 (2)
Ni-S(1)-C(2)	96.1 (2)	Ni-S(2)-C(8)	95.8 (2)
S(1)-C(2)-C(1)	118.7 (5)	S(2)-C(8)-C(9)	119.2 (5)
C(1)-C(2)-N(1)	117.4 (7)	C(9)-C(8)-N(4)	116.9 (6)
S(1)-C(2)-N(1)	123.9 (5)	S(2)-C(8)-N(4)	123.9 (6)
C(2)-N(1)-N(2)	112.7 (6)	C(8)-N(4)-N(3)	112.9 (5)
Ni-N(2)-N(1)	119.6 (3)	Ni-N(3)-N(4)	119.7 (3)
Ni-N(2)-C(3)	127.3 (4)	Ni-N(3)-C(6)	127.8 (5)
N(1)-N(2)-C(3)	113.0 (5)	N(4)-N(3)-C(6)	112.4 (5)
N(2)-C(3)-C(5)	120.6 (6)	N(3)-C(6)-C(5)	120.0 (5)
N(2)-C(3)-C(4)	122.8 (5)	N(3)-C(6)-C(7)	123.0 (6)
C(4)-C(3)-C(5)	116.6 (4)	C(7)-C(6)-C(5)	116.7 (4)
C(3)-C(5)-O	117.0 (6)	C(6)-C(5)-O	116.5 (5)
C(3)-C(5)-C(6)	126.4 (4)		

Table IX. Distances (Å) of the Atoms from the Least-Squares Planes Calculated for the Three Complexes[a]

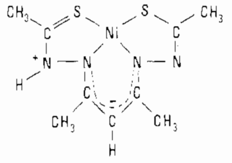
	[Ni((tah)$_2$acacH)]·CH$_3$CN, I			
atom	molecule 1	molecule 2	(C$_4$H$_9$)$_4$N-[Ni((tah)$_2$-acac)], II	[Ni((tah)$_2$-acacO)], III
Ni	−0.011	−0.022	0.007	−0.003
C(1)	−0.033	0.142	−0.048	−0.069
C(4)	−0.007	−0.014	0.020	0.005
C(7)	−0.093	−0.123	0.024	0.079
C(9)	0.061	0.048	−0.009	−0.085
S(1)*	−0.081	−0.108	0.048	0.003
C(2)*	0.015	0.035	−0.018	−0.015
N(1)*	0.037	0.072	−0.031	0.014
N(2)*	0.030	0.019	−0.008	0.035
C(3)*	0.016	−0.001	0.002	0.007
C(5)*	−0.023	−0.047	0.025	−0.089
C(6)*	−0.037	−0.051	0.007	0.046
N(3)*	−0.016	0.012	0.005	0.023
N(4)*	0.006	0.045	−0.014	0.021
C(8)*	0.043	0.042	−0.020	−0.018
S(2)*	0.010	−0.018	0.003	−0.027
O				−0.336

[a] The atoms marked with an asterisk are those used to define the least-squares plane.

symmetry. The two independent molecules of [Ni((tah)$_2$acacH)] do not show significant differences in their corresponding bond lengths and bond angles, but each complex appears to have systematic differences in the molecular dimensions of the two halves of the molecule even in view of the relatively high standard deviations. The averaged molecular dimensions for the complexes, I–III, are shown in Figures 2, 4, and 5.

The three nickel complexes all have a planar arrangement of the ligating atoms around the metal ion. Table IX lists the deviation of the heavy atoms from the least-squares planes defined by the ligating atoms.

The thioacethydrazonato parts of the ligands are almost identical in the structures of [Ni((tah)$_2$acac)]$^-$, [Ni((tah)$_2$acacO)], and in half of each of the molecules of [Ni((tah)$_2$acacH)]. In the last structure, the other half of the two independent molecules has different dimensions. The C–S distance is shorter than observed in the other cases (1.68 Å vs. 1.74 Å), and the C–N distance is longer (1.32 Å vs. 1.29 Å). These changes in the molecular dimensions could indicate that the complex I is present in another tautomeric form (vide infra). The same conclusion is reached when the acetylacetone parts of the ligand in the acid and in the tetrabutylammonium salt are compared. From Tables V and VI it is apparent that the bond lengths are very similar. Furthermore, only one peak corresponding to a hydrogen atom was found close to C(5). It has been impossible to locate the last hydrogen atom in the complex. It seems likely that the hydrogen atom is bonded to N(4) as shown in structure IV. This tautomeric representation is expected to enhance the C–S double bond character in agreement with the found short C–S bond length.



IV

This information can be supplemented with ^{1}H NMR spectroscopic results. Owing to low solubility of [Ni((tah)$_2$acacH)] in most solvents, we have performed measurements with [2,4-pentanedione bis(phenylacet thiohydrazonato)]nickel(II) and [3-methyl-2,4-pentanedione bis(thioacethydrazonato)]nickel(II) in CDCl$_3$, CD$_2$Cl$_2$, and (CD$_3$)$_2$SO. The latter complex has in all solvents a methyl signal split into a doublet, and this proves that the acid hydrogen atom must reside on the same carbon atom as the methyl group. However, the former complex has in CDCl$_3$ and CD$_2$Cl$_2$ a spectrum with δ_{NH} = 10.1 and δ_{CH} = 3.9 which is only compatible with a structure analogous to IV.

It thus seems likely that [Ni((tah)$_2$acacH)] indeed has the structure IV although the X-ray result is not quite conclusive.

The acetonitrile molecules in [Ni((tah)$_2$acacH)]·CH$_3$CN are situated between two nitrogen atoms from different molecules. The contact distances N(5)′–N(4)′ = 2.76 Å, N(5)′–N(1) = 2.96 Å, N(5)–N(1)′ = 2.93 Å, and N(5)–N(4) = 2.85 Å can be understood by assuming that each acetonitrile is involved in a hydrogen bond to N(4) and in an electrostatic interaction with N(1) in agreement with the proposed structure IV.

The delocalization within the acetylacetone part of the ligand found in these two structures is in great contrast to the related dimensions in [Ni((tah)$_2$acacO)]. It is remarkable that in the last structure all the distances within the ligand can be interpreted as corresponding to either single or double bonds. The C(3)–C(5) distance of 1.48 Å in III has a value characteristic for a sp^2 hybrid single bond, and it is grossly different from the C(3)–C(5) distance found in I and II of 1.39 Å.

Comparisons with Related Complexes. Table X contains structural characteristics of free thiosemicarbazones and nickel complexes with thiosemicarbazones and thioacethydrazones. It is apparent that although the coordination of nickel is very similar in the planar complexes **1**–**7** of Table X, the trend is that the Ni–S and Ni–N bond lengths observed in the three structures reported here are slightly shorter than the corresponding distances in **1**, **2**, **6**, and **7**. The five- and six-coordinated complexes **8**–**10** of Table X have considerably longer Ni–S and Ni–N bond lengths.

Comparable bond lengths in the thiosemicarbazone and thioacethydrazone moieties in **1**–**10** are relatively alike. The C–S bonds have values between 1.67 and 1.75 Å suggesting that this bond has a considerable amount of double bond character. The sulfur atoms in the complexes thus have presumably little negative charge, and this could explain why attempts to alkylate, e.g., [Ni((tah)$_2$acacO)] with 1,3-dibromopropane, were unsuccessful[1] while complexes of formally thiolate ligands have been S-alkylated.[34,35] Tasker[36,37] has

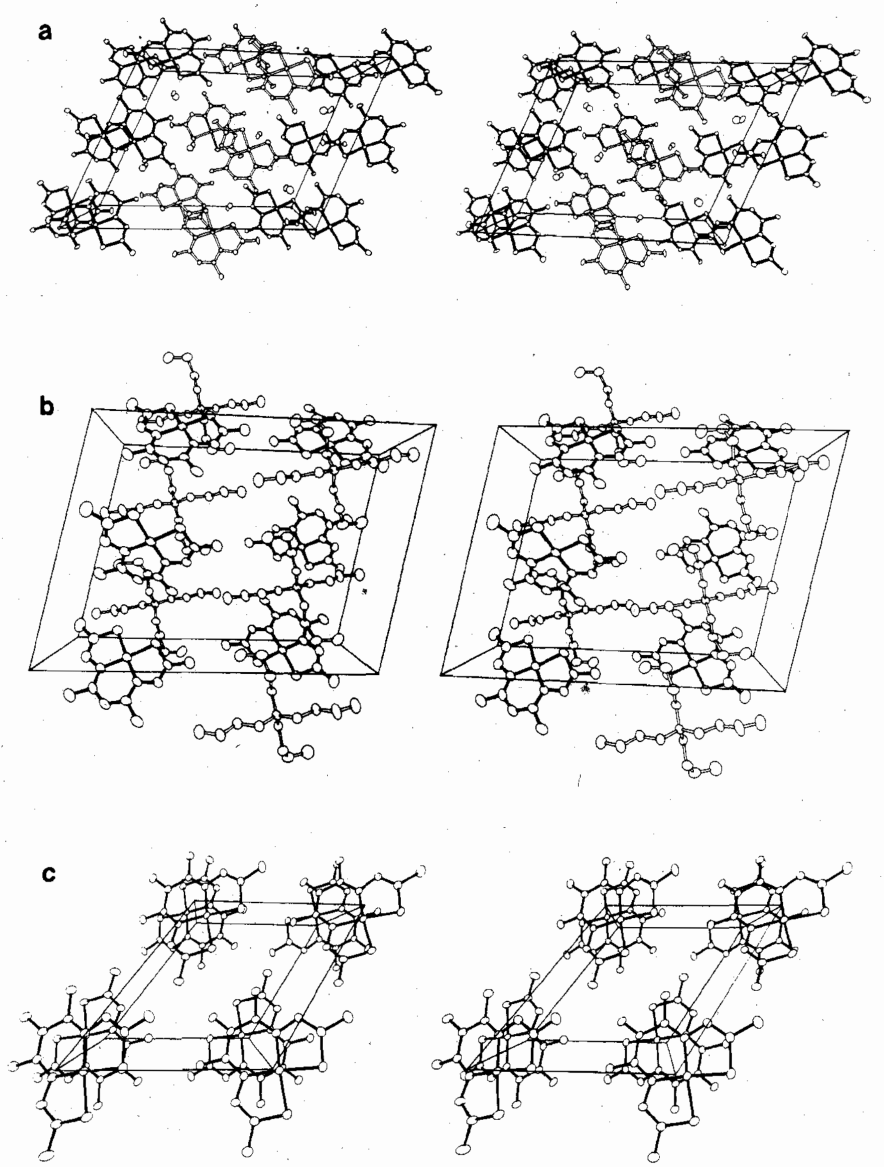


Figure 1. (a) Stereopair illustrating the packing of [Ni((tah)$_2$acacH)]·CH$_3$CN viewed from the *b* axis. The molecules drawn with open bonds are labeled as molecule 1. The thermal ellipsoids are drawn to enclose 25% probability. (b) Stereoview of the packing in (C$_4$H$_9$)$_4$N[Ni((tah)$_2$acac)] viewed from the *b* axis. The thermal ellipsoids are enclosing 25% probability. (c) Stereoview of the packing in [Ni((tah)$_2$acacO)] seen perpendicular to the $\bar{c}$*, $\bar{b}$* plane. The thermal ellipsoids enclose 25% probability.

Table X

no.	complex	Ni-S, Å	Ni-N, Å	S-C, Å	C-N(N), Å	N-N, Å	N=C, Å	ref
1	[Ni(tah-acetophenone)$_2$]	2.150	1.935	1.737	1.285	1.428	1.298	*a*
2	[Ni((path)$_2$(butanedione))]	2.151	1.853	1.746	1.295	1.393	1.302	*b*
3	[Ni((tah)$_2$acacH)]	2.127	1.846	1.677	1.318	1.404	1.351	*c*
		2.120	1.862	1.722	1.273	1.415	1.321	
4	[Ni((tah)$_2$acac)]	2.146	1.855	1.718	1.292	1.402	1.329	*c*
5	[Ni((tah)$_2$acacO)]	2.143	1.898	1.719	1.296	1.406	1.308	*c*
6	[Ni(4-Me(tsc)$_2$-2,5-hexanedione)]	2.16	1.91	1.76	1.31	1.41	1.33	*d, e*
		2.18	1.98	1.76	1.30	1.40	1.30	
7	[Ni((tsc)$_2$(phthalaldehyde))]	2.16	1.92	1.72	1.35	1.41	1.33	*d, e*
		2.17	1.93	1.74	1.32	1.41	1.33	
8	[Ni((tsc)$_2$-1-formylisoquinoline)]	2.42	2.02	1.73	1.33	1.36	1.29	*f*
9	[Ni(Htsc-acetone)$_2$Cl]$^+$	2.30	2.13	1.70	1.32	1.39	1.28	*g*
10	[Ni(Htsc-acetone)$_2$NO$_3$]$^+$	2.33	2.12	1.66	1.34	1.40	1.30	*g*
11	Htsc-2-formylthiophene			1.695	1.345	1.374	1.286	*h*
12	Htsc-4-formylpyridine			1.678	1.354	1.365	1.275	*i*
13	Htsc-acetone			1.690	1.342	1.398	1.286	*j*
14	Htsc-5-hydroxy-2-formylpyridine			1.706	1.336	1.379	1.270	*j*

[a] S. Larsen, *Acta Chem. Scand., Ser. A*, **28**, 779 (1974). [b] F. Hansen and S. Larsen, *ibid.*, **31**, 825 (1977). [c] This work. [d] N. A. Bailey, S. E. Hull, C. J. Jones, and J. A. McCleverty, *Chem. Commun.*, 124 (1970). [e] M. M. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975). [f] M. Mathew and G. J. Palenik, *J. Am. Chem. Soc.*, **91**, 6310 (1969). [g] M. Mathew, G. J. Palenik, and G. R. Clark, *Inorg. Chem.*, **12**, 446 (1973). [h] M. Mathew and G. J. Palenik, *Acta Crystallogr., Ser. B*, **27**, 59 (1971). [i] R. Restivo and G. J. Palenik, *ibid.*, **26**, 1397 (1970). [j] G. J. Palenik, D. F. Rendle and W. S. Carter, *ibid.*, **30**, 2390 (1974).

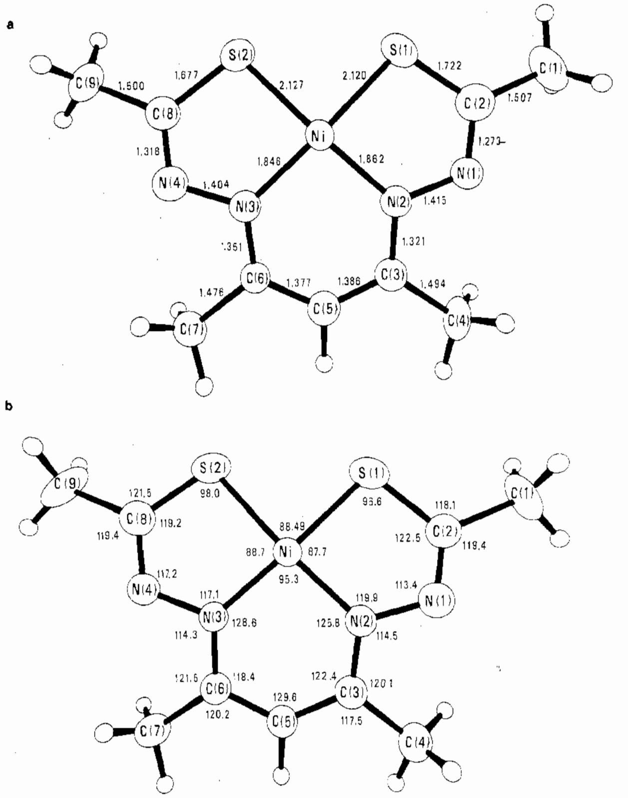


Figure 2. Structure of the two molecules of [Ni((tah)$_2$acacH)]. The averaged bond lengths are displayed in part a and the average bond angles on the molecule in part b. The thermal ellipsoids enclose 50% probability.

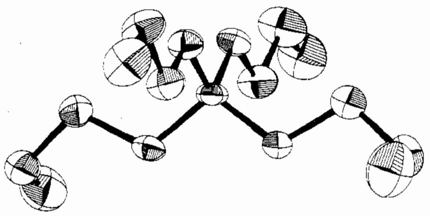


Figure 3. ORTEP drawing of the tetra-*n*-butylammonium ion in $(C_4H_9)_4N$[Ni((tah)$_2$acac)] illustrating the C_{2v} symmetry of the ion. The thermal ellipsoids enclose 25% probability.

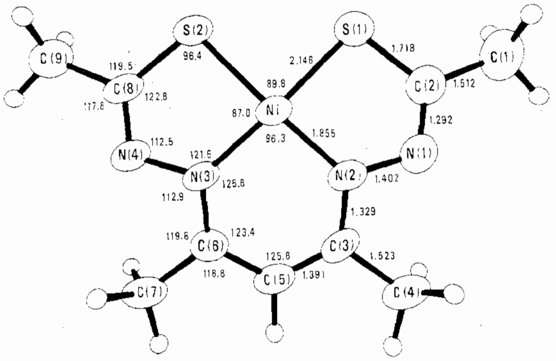


Figure 4. Structure of the anion in $(C_4H_9)_4N$[Ni((tah)$_2$acac)] showing the averaged bond lengths and bond angles. The thermal ellipsoids enclose 25% probability.

determined the structure of two thioether complexes of a composition similar to the expected reaction product between [Ni((tah)$_2$acac)] and 1,3-dibromopropane. The Ni–S distances are 2.16–2.18 Å in these thioether complexes.

Relations between Structural and Spectral Results. The marked color differences between nickel(II) complexes with rather similar ligands were important for the initiation of this work. However, the structural results do not directly throw light on this problem. As demonstrated above, conjugation from one thioacyl part to the other in [Ni((tah)$_2$acac)]$^-$ is evident from the values of the C–C and N–C bond lengths in the N–C–C–C–N framework. We have given evidence for a similar cross conjugation in the corresponding acid, and these two compounds both have orange colors. The maximum of the envelope of a weak absorption considered to be largely due to the d–d transitions is found at 19 500 cm^{-1}. The first allowed transition assumed to be a more or less internal $\pi \rightarrow \pi^*$ transition has its maximum at 25 000 cm^{-1}. The green complexes [Ni((tah)$_2$acacO)] and [Ni((path)$_2$(diacetyl))] may of course also possess cross conjugation between the π systems of the thioacyl units; however, in these structures the C–C and C–N bond lengths do not deviate much from ideal values for single bonds and double bonds, respectively. The green color is caused by a weak absorption band (d–d transitions) at ca. 16 000 cm^{-1}. The first $\pi \rightarrow \pi^*$ transition is found near 28 000 cm^{-1} for both complexes.

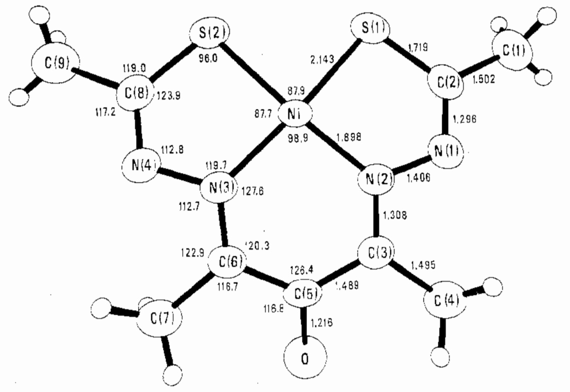


Figure 5. Structure of [Ni((tah)$_2$acacO)] showing the averaged bond lengths and bond angles. The thermal ellipsoids enclose 50% probability.

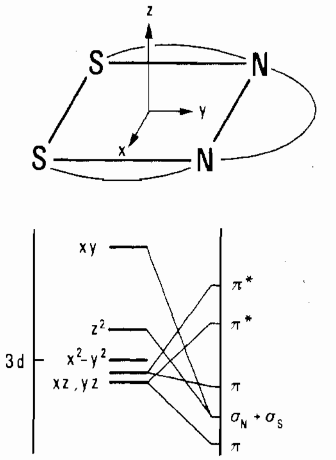


Figure 6. A schematic drawing of a Ni(II) complex of a quadridentate ligand with a coordinate system inserted with the origin at the Ni site and with y as a twofold axis of symmetry. The qualitative MO diagram demonstrates that the energy difference between the empty xy orbital and the average of the remaining filled d orbitals is efficiently changed by a relative change of the σ rather than the π interaction.

The green compounds [Ni((tah)$_2$(diacetyl))] and [Ni((tah)$_2$acacO)] have 10 and 12 π orbitals containing 10 and 12 electrons, respectively. [Ni((tah)$_2$acac)]$^-$ has 11 orbitals with 12 electrons, and the smaller $\pi \rightarrow \pi^*$ excitation energy found for the latter complex relative to the former two is in accordance with the usual trend for polyenes of varying number of electrons.

The d–d band is only weakly structured in these complexes, but in some cases three components are distinguishable corresponding to transitions from the manifold of filled d orbitals of Figure 6 to the σ^* orbital of xy symmetry. The σ interaction between the xy and z^2 d orbitals with the ligand σ orbitals could be the same in the green and the orange complexes. Then the difference in the d–d absorption maximum for the two groups of complexes would be determined by a different amount of interaction between the yz, zx d orbitals and the ligand π orbitals. The most important interaction will be with the lowest lying empty π^* orbital which stabilizes the d_π orbitals. The stabilization must be most pronounced in the complexes having an even number of ligand π orbitals only half filled, i.e., in the green complexes. We would therefore expect the d–d transitions in the green complexes to occur at a higher energy than in the orange complexes. The opposite is observed, and we interpret this as an indication of significantly different σ interactions in the two groups of complexes. This effect is not evident from the variation of bond lengths.

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Registry No. I, 68926-71-6; II, 65533-07-5; III, 65533-14-4.

Supplementary Material Available: Tables A1–A3, hydrogen atom positional and thermal parameters for structures I–III, and Tables A4–A6, listings of $10|F_c|$ and $10|F_o|$ for all three compounds (24 pages). Ordering information is given on any current masthead page.

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Coordination of Metal Carbonyl Anions to Triphenylaluminum, -gallium, and -indium and the Crystal Structure of Tetraethylammonium Triphenyl((η^5-cyclopentadienyl)dicarbonyliron)aluminate(*Fe–Al*)[1]

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Complexes of triphenylmetal acceptors, Ph_3E, where E is Al, Ga, or In, with metal carbonyl anions, $m^- = CpFe(CO)_2^-$, $CpW(CO)_3^-$, $Co(CO)_4^-$, and $Mn(CO)_5^-$, where $Cp = \eta^5\text{-}C_5H_5$, were prepared by combining the donor salt with the acceptor in dichloromethane or, in the case of $CpFe(CO)_2^-$, in tetrahydrofuran. The following crystalline complexes were isolated: $Et_4N^+Ph_3EFe(CO)_2Cp^-$ (E = Al, Ga, and In), $((n\text{-}Bu)_4N^+Ph_3E)CpW(CO)_3^-$ (E = Al and In), $(Ph_3P)_2N^+Ph_3InCo(CO)_4^-$, and $(n\text{-}Pr)_4N^+Ph_3InMn(CO)_5^-$. The title compound crystallized in space group $P2_1/c$ with $a = 10.507$ (3) Å, $b = 15.254$ (4) Å, $c = 18.892$ (4) Å, and $\beta = 92.63$ (2)°. The complex possesses a direct Fe–Al bond of length 2.510 (2) Å between the donor and acceptor moieties. This bond, the first between iron and aluminum in an organometallic complex, appears to have predominantly single bond character. By analysis of infrared spectroscopic data (ν_{C-O}) the presence of a metal–metal bond was revealed in all complexes except that of $(n\text{-}Bu)_4N^+CpW(CO)_3^-$ with Ph_3Al in which case the oxygen atom of a carbonyl ligand is the site of Lewis basicity in a $WC{\equiv}OAl$ link. Dichloromethane solutions of $(n\text{-}Bu)_4N^+Ph_3GaCpW(CO)_3^-$ contain, in addition to uncomplexed $CpW(CO)_3^-$, two isomeric complexes: a metal–metal bonded species analogous to the corresponding Ph_3In complex and a C- and O-bonded adduct of the type found in the Ph_3Al complex. Complexes of Ph_3Ga and, especially, of Ph_3Al with $Co(CO)_4^-$ and $Mn(CO)_5^-$ were thermally unstable. Approximate formation constants for the complexes were estimated from IR band intensities and the relative magnitudes can be rationalized in terms of the principle of hard and soft acids and bases.

Introduction

Transition-metal carbonyl anions, m^-, have been used widely for the synthesis of numerous derivatives m–X in which the metal, M, as the site of Lewis basicity, forms a direct covalent M–X bond.[2,3] With certain acceptors, however, the interposition of a carbonyl group generates an $MC{\equiv}OX$ sequence

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