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Synthesis, Properties, and Structural Characterization of Dinuclear Halogen-Bridged Nickel(I) Complexes with Tris(2-diphenylarsinoethyl)amine

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Dinuclear nickel(I) complexes with the tetradentate ligand tris(2-diphenylarsinoethyl)amine (nas_3), of formula $[Ni_2X(nas_3)_2]BPh_4$, X = Br, I, were synthesized by reduction of the five-coordinated complexes $[NiX(nas_3)]BPh_4$. The structure of the $[Ni_2I(nas_3)_2]BPh_4 \cdot 3THF$ compound was determined by x-ray analysis using diffractometric data. The crystals are monoclinic, space group $C2/c$, with cell dimensions $a = 15.476$ (2) Å, $b = 25.820$ (3) Å, $c = 27.209$ (3) Å, and $\beta = 96.42$ (2)°. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.061 over the 1588 independent observed reflections. The structure consists of dinuclear $Ni_2I(nas_3)_2^+$ cations, of tetraphenylborate anions, and of interposed tetrahydrofuran molecules. Each nickel atom is bonded to the four donor atoms of the nas_3 ligand and to the shared bridging iodine atom which lies on a center of symmetry. The chromophore may be considered to be formed by two trigonal bipyramids with a common vertex. The long axial distances Ni–I = 2.994 (4) Å and Ni–N = 2.31 (2) Å are noteworthy. The magnetic behavior of these complexes suggests the existence of antiferromagnetic exchange between the two nickel atoms, involving the halogen atom bridge.

Introduction

From reactions of the tripod ligand tris(2-diphenylarsinoethyl)amine, nas_3, with nickel(II) halides five-coordinated complexes of nickel(II), having the general formula $[NiX(nas_3)]BPh_4$, X = Br, I, are obtained.[1] If $[NiX(nas_3)]BPh_4$ or the nickel(II) halides and the ligand are reacted with $NaBH_4$ in the $Ni:NaBH_4$ ratio 1:1, nickel(I) complexes with the formula $NiX(nas_3)$, X = Cl, Br, I, are obtained.[2] If the ratio $Ni:NaBH_4$ is limited to 1:0.5, dinuclear $[Ni_2X(nas_3)_2]BPh_4$ nickel(I) complexes are obtained (X = Br, I).

These compounds have been fully characterized by the usual methods. A complete x-ray structural analysis has been carried out on a tetrahydrofuran adduct of the iodo derivative.

A short preliminary communication on this work has already appeared.[3]

Experimental Section

Solvents were dried before use by standard methods. All reactions were run under a nitrogen atmosphere. The ligand tris(2-diphenylarsinoethyl)amine, nas_3, was prepared as already described.[4] Conductivity and spectrophotometric measurements were carried out using methods described elsewhere.[5] Magnetic susceptibilities were measured using the Gouy method, the apparatus and experimental technique being those previously described.[6] Diamagnetic corrections were calculated using Pascal's constants.[7]

Synthesis of the Complexes. $[Ni_2Br(nas_3)_2]BPh_4$. A solution of $NaBH_4$ (0.5 mmol) and $NaBPh_4$ (0.5 mmol) in absolute ethanol (20 ml) was slowly added to a solution of $[NiBr(nas_3)]BPh_4$ (1 mmol) in methylene chloride (10 ml) and tetrahydrofuran (10 ml). The resulting solution was concentrated at room temperature until orange crystals precipitated. The compound was filtered and washed with toluene and petroleum ether. Anal. Calcd for $[Ni_2Br(nas_3)_2]BPh_4 \cdot 3THF$, $C_{120}H_{128}N_2As_6BBrNi_2O_3$: C, 62.6; H, 5.6; N, 1.2; As, 19.5; Br, 3.5; Ni, 5.1. Found: C, 62.5; H, 5.5; N, 1.2; As, 19.3; Br, 3.2; Ni, 5.1.

$[Ni_2I(nas_3)_2]BPh_4$. This garnet red compound was prepared in the same manner as the previous compound starting from $[NiI(nas_3)]BPh_4$ in tetrahydrofuran (30 ml). Anal. Calcd for $[Ni_2I(nas_3)_2]BPh_4 \cdot 3THF$, $C_{120}H_{128}N_2As_6BINi_2O_3$: C, 61.3; H, 5.5; N, 1.2; As, 19.1; I, 5.4; Ni, 5.0. Found: C, 61.2; H, 5.5; N, 1.2; As, 19.0; I, 5.0; Ni, 5.1.

Collection and Reduction of X-Ray Intensity Data. The garnet red crystals of $[Ni_2I(nas_3)_2]BPh_4 \cdot 3THF$ are plate-shaped. The crystal used for the x-ray analysis had dimensions 0.25 × 0.20 × 0.08 mm. Cell parameters were determined at room temperature (about 22 °C) by carefully measuring the setting angles of 20 reflections on a Philips PW 1100 diffractometer. Details of crystal data and data collection are given in Table I. The standard deviations on the intensities were calculated as described elsewhere,[8] using a value of the instability factor k of 0.04. The number of observed reflections (1588) is rather low with respect to the large number of independent nonhydrogen atoms of the structure. However a refinement carried out at the end of the analysis using the reflections having $I \geq 2\sigma(I)$ was unsuccessful. The observed reflections were corrected for Lorentz and polarization effects. An absorption correction was applied using a numerical method:[9] the transmission factors were found to range from 0.70 to 0.82. Atomic scattering factors for I, As, Ni, N, C, and B and those for hydrogen atoms (all in the neutral state) were taken from ref 10 and 11, respectively. Corrections for anomalous dispersion effects for iodine, arsenic, and nickel atoms[12] were applied in the refinement stage.

Table I. Crystal Data and Data Collection Details

Mol formula	$C_{120}H_{128}O_3BAs_6N_2Ni_2I$
Mol wt	2351.0
a, Å	15.476 (2)
b, Å	25.820 (3)
c, Å	27.209 (3)
β, deg	96.42 (2)
d_{obsd}(by flotn), g cm^{-3}	1.46
d_{calcd}, g cm^{-3}	1.454
V, Å^3	10 804.2
Z	4
Space group	$C2/c$
Abs coeff (Mo Kα), cm^{-1}	26.30
λ(Mo Kα), Å	0.7093
Monochromator	Flat graphite crystal
Takeoff angle, deg	2.0
Method	ω–2θ
Scan speed	0.07°/s in a range of 0.7°
Background time	7 s on each side of the peak
Standards	3 every 30 min
Max dev of standards	10%
2θ limit	$6° \leq 2\theta \leq 40°$
No. of data	5511
No. of obsd data ($I \geq 3\sigma(I)$)	1588

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis yielded the positional parameters of the iodine, nickel, and arsenic atoms. The other nonhydrogen atoms, except those belonging to the tetrahydrofuran solvent molecules, were located from successive three-dimensional F_o Fourier maps. The solvent molecules appeared only in a ΔF Fourier synthesis calculated before the refinement cycle. These molecules appeared to be affected by disorder, and it was not possible, even in an advanced stage of refinement, to find the position of one of the atoms of a solvent molecule. Since it was not possible to distinguish between oxygen and carbon atoms for the tetrahydrofuran molecules, all the atoms of the solvent were introduced in the subsequent calculations as carbon atoms. Refinement was performed by use of the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[13] The function minimized was $\sum w(|F_o| - |F_c|)^2$, in which w is the weight assigned to the F_o values according to the expression $w = 1/(\sigma(F_o))^2$. Two cycles of refinement with individual isotropic temperature factors for all of the atoms were carried out. The hydrogen atoms of the nas_3 ligand and of the BPh_4^- ion were introduced in calculated positions (C–H = 0.95 Å) and were

Table II. Positional Parameters (×10^4), Anisotropic Temperature Factors^a (×10^3), and Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	5000	5000	5000	43 (2)	61 (2)	43 (2)	−3 (2)	1 (2)	−7 (2)
As(1)	3120 (2)	4949 (1)	3910 (1)	35 (2)	46 (2)	31 (2)	5 (2)	4 (2)	1 (2)
As(2)	5407 (2)	4217 (1)	3810 (1)	34 (2)	53 (3)	38 (2)	8 (2)	8 (2)	0 (2)
As(3)	3721 (2)	3644 (1)	4708 (1)	38 (2)	43 (2)	36 (2)	1 (2)	6 (2)	0 (2)
Ni	4133 (2)	4318 (1)	4202 (1)	34 (2)	57 (3)	30 (3)	8 (2)	7 (2)	3 (2)
N	3492 (14)	3808 (8)	3567 (7)	71 (18)	40 (17)	19 (14)	−1 (14)	10 (13)	−3 (12)

^{a} Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$.

not refined (an overall B of 5 Å^2 was used). Refinement was then continued using anisotropic temperature factors for iodine, arsenic, nickel, and nitrogen atoms and isotropic factors for the other atoms. Two refinement cycles gave a conventional R factor of 0.061 and a weighted R factor, defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.074. A final ΔF Fourier synthesis did not show any remarkable feature, except for some residual electronic density in the region of the solvent molecules. We noticed some large ΔF values at the end of refinement: they can be accounted for by this residual electronic density. The final values of the parameters and their standard deviations are reported in Tables II and III.

Results and Discussion

The iodo derivative is quite air stable, while the bromo derivative decomposes in air. Both compounds, which crystallize with three molecules of tetrahydrofuran, are slightly soluble in tetrahydrofuran, methylene chloride, and 1,2-dichloroethane; in the last solvent they behave as 1:1 electrolytes. They slowly decompose in solution even in an inert atmosphere.

As the ratio Ni(I):$NaBH_4$ is 1:0.5 for the formation reactions of both complexes, the reduction of the metal must be attributed only in part to the tetrahydroborate ion. It seems therefore likely that also the tetraphenylborate ion acts as reducing agent completing the reduction of nickel(II) to nickel(I). This reducing ability of the tetraphenylborate ion toward 3d metals has already been found in the formation of nickel complexes with 1,8-naphthyridine.[14] It was not possible to define the reaction stoichiometry, but a reasonable scheme for this reduction could be that found for copper(II) chloride[15]

$$2BPh_4^- \rightarrow 2BPh_3 + Ph_2 + 2e^-$$

in which Ph_2 signifies diphenyl.

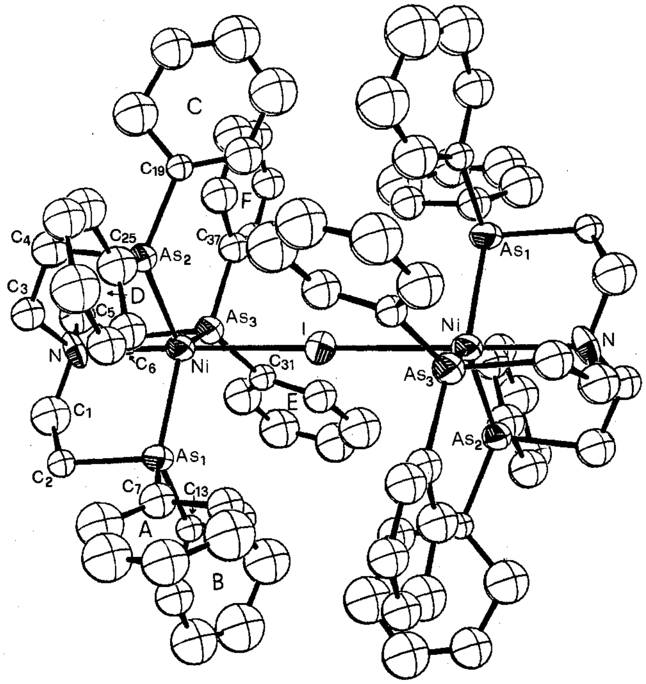

Figure 1. ORTEP diagram of the $Ni_2I(nas_3)_2^+$ cation.

The structure of the iodo derivative consists of dinuclear $Ni_2I(nas_3)_2^+$ cations, of tetraphenylborate anions, and of interposed tetrahydrofuran solvent molecules. Each nickel atom is bonded to the four donor atoms of the nas_3 ligand and to the shared bridging iodine atom. The iodine atom lies on a center of symmetry and therefore the Ni–I–Ni bridge is strictly linear. The chromophore can be considered to be formed by two trigonal bipyramids sharing a vertex. The nickel atom is only 0.21 Å out of the equatorial plane, toward the iodine atom. A perspective view of the complex cation is shown in Figure 1. Table IV lists selected intramolecular distances and angles with their estimated standard deviations. The two axial distances Ni–I, 2.994 (4) Å, and Ni–N, 2.31 (2) Å, are significantly longer than the Ni–I and Ni–N distances found in five-coordinated nickel(II) complexes with tripod ligands,[2,16] and furthermore these distances are remarkably longer than the sums of the covalent radii of the elements: Ni, 1.15 Å; I, 1.33 Å; N, 0.70 Å.[17] The lengthening of these axial distances, compared with those of nickel(II) trigonal-bipyramidal complexes, can be explained considering the splitting of the 3d orbitals in C_{3v} symmetry.[18] According to this pattern the a_1' (d_{z^2}) orbital is that having the highest energy, and therefore it is empty for a d^8 ion, such as nickel(II), while it is occupied by one electron for a d^9 ion, such as nickel(I). This may account for the increase of the apical distances in nickel(I) trigonal-bipyramidal complexes with respect to nickel(II) complexes. The large value of the Ni–I distance, which is longer by 0.5 Å than the sum of covalent radii, can be attributed mainly to steric factors: the bulky phenyl groups on opposite parts of the dinuclear compound may prevent the Ni(nas_3) moieties from getting closer to each other, as can be observed from the short contact distances H(29)···C(28) = 2.87, H(29)···C(40) = 2.87, H(29)···C(41) = 2.91, H(33)···C(10) = 2.82, and H(33)···C(11) = 2.93 Å (the numbering of the hydrogen atoms is that of the carbon atoms to which they are attached). These distances are very close to the sum of the van der Waals radii of carbon and hydrogen, 1.70 and 1.20 Å, respectively.[19] A long Co–I-(bridge) distance, 2.85 Å, has been found also in a bioctahedral cobalt(II) complex, which is diamagnetic following superexchange involving the iodine bridging atom.[20] Also for this complex steric impediments between phenyl rings belonging to ligand molecules could be invoked to account for the long distance.

On the other hand, the three Ni–As equatorial distances, 2.35 Å (average), appear normal, when they are compared to the Ni–As distances found in the $[Ni(C_6H_5)(nas_3)]BPh_4$ complex, 2.34 Å (average).[2] Also the other distances and angles in the cationic complex and in the tetraphenylborate ion, which has the boron atom on the twofold axis, appear normal.

The magnetic susceptibilities of the compounds, which have been found to be independent of the magnetic field strength, have been investigated over the range 84–290 K. The graph of μ_{eff} (per nickel atom) vs. T is reported in Figure 2. μ_{eff} for the iodo derivative has a constant value in the range of the measurements while μ_{eff} for the bromo derivative has a constant value from 84 to 200 K but above this temperature

Table III. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors ($\times 10^3$), and Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U, Å^2
C(1)	2994 (16)	4146 (11)	3202 (10)	46 (8)
C(2)	2436 (18)	4541 (12)	3390 (11)	59 (10)
C(3)	4139 (19)	3525 (13)	3317 (12)	69 (11)
C(4)	4926 (16)	3853 (9)	3199 (9)	33 (8)
C(5)	2878 (19)	3436 (12)	3776 (12)	60 (10)
C(6)	3240 (18)	3156 (12)	4190 (12)	55 (10)
C(7)	3422 (18)	5522 (11)	3523 (11)	59 (10)
C(8)	4293 (17)	5602 (11)	3428 (11)	51 (9)
C(9)	4557 (17)	5970 (11)	3142 (11)	51 (9)
C(10)	3974 (21)	6353 (14)	2934 (12)	81 (11)
C(11)	3082 (18)	6281 (12)	3020 (11)	60 (9)
C(12)	2820 (18)	5904 (13)	3291 (12)	67 (10)
C(13)	2260 (16)	5249 (10)	4289 (10)	29 (8)
C(14)	1357 (21)	5200 (12)	4108 (12)	79 (11)
C(15)	771 (20)	5428 (13)	4448 (13)	70 (11)
C(16)	1028 (25)	5666 (14)	4860 (15)	91 (12)
C(17)	1871 (25)	5684 (14)	4999 (13)	94 (12)
C(18)	2480 (19)	5480 (12)	4704 (13)	58 (10)
C(19)	6284 (15)	3754 (10)	4032 (9)	32 (8)
C(20)	7048 (20)	3651 (15)	3793 (11)	61 (10)
C(21)	7615 (22)	3276 (15)	3952 (15)	94 (13)
C(22)	7613 (24)	3071 (15)	4403 (17)	111 (14)
C(23)	6907 (24)	3164 (15)	4747 (15)	99 (13)
C(24)	6313 (19)	3513 (12)	4483 (12)	75 (10)
C(25)	6105 (17)	4730 (11)	3552 (12)	50 (9)
C(26)	6197 (20)	4842 (12)	3066 (14)	83 (12)
C(27)	6720 (22)	5233 (15)	2937 (13)	88 (12)
C(28)	7109 (21)	5567 (14)	3214 (15)	77 (12)
C(29)	7046 (23)	5510 (15)	3722 (16)	94 (13)
C(30)	6572 (16)	5110 (11)	3892 (10)	50 (9)
C(31)	4432 (16)	3211 (12)	5171 (10)	35 (8)
C(32)	5037 (19)	3438 (11)	5502 (12)	53 (9)
C(33)	5565 (22)	3151 (16)	5858 (14)	87 (12)
C(34)	5476 (22)	2639 (16)	5825 (14)	82 (12)
C(35)	4909 (23)	2348 (14)	5497 (14)	83 (12)
C(36)	4399 (20)	2692 (15)	5151 (12)	70 (11)
C(37)	2717 (17)	3694 (12)	5096 (10)	44 (9)
C(38)	2128 (18)	4073 (12)	4969 (11)	61 (10)
C(39)	1353 (20)	4115 (13)	5231 (13)	75 (11)
C(40)	1237 (17)	3745 (12)	5561 (11)	51 (9)
C(41)	1782 (19)	3374 (11)	5682 (11)	53 (9)
C(42)	2501 (18)	3336 (11)	5416 (11)	55 (9)
C(43)	211 (17)	3605 (12)	2064 (11)	46 (9)
C(44)	−218 (20)	3677 (14)	1556 (14)	80 (11)
C(45)	42 (22)	3994 (13)	1200 (13)	77 (11)
C(46)	696 (22)	4341 (14)	1295 (13)	78 (11)
C(47)	1149 (20)	4357 (13)	1767 (14)	67 (11)
C(48)	865 (21)	4025 (14)	2119 (13)	80 (12)
C(49)	839 (19)	2856 (13)	2683 (13)	62 (10)
C(50)	783 (21)	2507 (13)	3045 (14)	64 (11)
C(51)	1485 (21)	2181 (13)	3224 (12)	63 (10)
C(52)	2229 (20)	2205 (13)	3014 (13)	66 (11)
C(53)	2335 (20)	2532 (13)	2651 (13)	70 (11)
C(54)	1633 (18)	2889 (12)	2450 (11)	64 (10)
B	0	3264 (18)	2500	33 (14)
C(55)[a]	5123 (34)	2169 (21)	1401 (25)	165 (20)
C(56)	3906 (43)	2043 (26)	1621 (27)	215 (27)
C(57)	4596 (41)	2231 (23)	1014 (23)	180 (23)
C(58)	3854 (39)	1825 (24)	1085 (26)	223 (25)
C(59)	4773 (72)	2241 (38)	1834 (40)	365 (50)
C(60)	5000	267 (46)	2500	345 (56)
C(61)	4119 (20)	592 (12)	2500 (12)	63 (11)

[a] Atoms of the tetrahydrofuran solvent molecules (see text).

increases slowly to reach ca. 1 μ_B at 290 K. These two complexes can be therefore considered essentially diamagnetic at low temperature, the residual value of μ_{eff} being attributable to paramagnetic impurities. In fact magnetic susceptibility slightly varies from sample to sample, but the plots obtained in each case are essentially the same as those reported in Figure 2, which is based upon the samples of lowest μ_{eff} in each case.

Table IV. Interatomic Distances (Å), Angles (deg), and Their Respective Standard Deviations

(A) Selected Bond Lengths

Ni–I	2.994 (3)	As(3)–C(6)	1.97 (3)
Ni–As(1)	2.337 (5)	As(3)–C(31)	1.93 (3)
Ni–As(2)	2.358 (5)	As(3)–C(37)	1.98 (3)
Ni–As(3)	2.352 (5)	N–C(1)	1.47 (3)
Ni–N	2.31 (2)	N–C(3)	1.46 (4)
As(1)–C(2)	1.97 (3)	N–C(5)	1.51 (4)
As(1)–C(7)	1.91 (3)	C(1)–C(2)	1.46 (4)
As(1)–C(13)	1.93 (3)	C(3)–C(4)	1.55 (4)
As(2)–C(4)	1.98 (2)	C(5)–C(6)	1.40 (4)
As(2)–C(19)	1.86 (2)	B–C(43)	1.54 (4)
As(2)–C(25)	1.89 (3)	B–C(49)	1.70 (4)

(B) Selected Bond Angles

I–Ni–As(1)	93.8 (1)	C(4)–As(2)–C(25)	101.4 (12)
I–Ni–As(2)	93.7 (1)	C(19)–As(2)–C(25)	98.3 (11)
I–Ni–As(3)	98.0 (1)	Ni–As(3)–C(6)	99.2 (9)
I–Ni–N	178.0 (5)	Ni–As(3)–C(31)	129.6 (8)
As(1)–Ni–As(2)	119.1 (2)	Ni–As(3)–C(37)	123.0 (9)
As(1)–Ni–As(3)	119.9 (2)	C(6)–As(3)–C(31)	103.7 (12)
As(1)–Ni–N	85.8 (5)	C(6)–As(3)–C(37)	99.6 (12)
As(2)–Ni–As(3)	118.6 (2)	C(31)–As(3)–C(37)	96.6 (11)
As(2)–Ni–N	84.8 (6)	Ni–N–C(1)	108.4 (15)
As(3)–Ni–N	83.9 (5)	Ni–N–C(3)	111.9 (16)
Ni–As(1)–C(2)	99.0 (9)	Ni–N–C(5)	108.6 (16)
Ni–As(1)–C(7)	122.1 (9)	C(1)–N–C(3)	108.4 (20)
Ni–As(1)–C(13)	125.0 (8)	C(1)–N–C(5)	109.1 (20)
C(2)–As(1)–C(7)	99.5 (12)	C(3)–N–C(5)	110.3 (22)
C(2)–As(1)–C(13)	104.5 (11)	N–C(1)–C(2)	117.4 (23)
C(7)–As(1)–C(13)	102.1 (12)	As(1)–C(2)–C(1)	109.4 (18)
Ni–As(2)–C(4)	100.2 (8)	N–C(3)–C(4)	114.7 (24)
Ni–As(2)–C(19)	122.8 (8)	As(2)–C(4)–C(3)	108.4 (18)
Ni–As(2)–C(25)	129.1 (9)	N–C(5)–C(6)	115.0 (23)
C(4)–As(2)–C(19)	99.2 (10)	As(3)–C(6)–C(5)	109.3 (21)

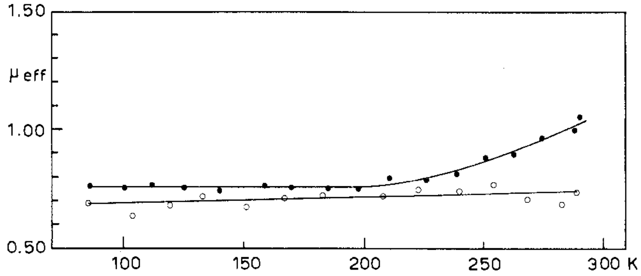

Figure 2. Variation with temperature of the magnetic moment μ_{eff} for Ni(I) in $[Ni_2Br(nas_3)_2]BPh_4$ (●) and in $[Ni_2I(nas_3)_2]BPh_4$ (○).

This magnetic behavior suggests that an antiferromagnetic exchange takes place between the two nickel atoms through the bridging halogen atom. Antiferromagnetic exchange between the two d^9 ions can arise from an intermixing of the d_{z^2} orbital of each nickel atom with a p_z orbital of the halide ion through a p_σ–a_1' pathway.[21] The different behavior of μ_{eff} vs. T for the two compounds above 200 K suggests that the coupling constant J between nickel atoms of the iodo derivative is greater than that in the bromo derivative. This is in agreement with the general finding that the exchange coupling constant becomes larger as the electronegativity of the anion decreases. The increasing μ_{eff} value with temperature above 200 K for the bromo derivative is probably due to the population of a thermally accessible triplet level. For this complex the values of g and J have been calculated fitting the Bleaney–Bowers[22] equation to the experimental susceptibility data by the use of a least-squares program. The best pair of values are 2.00 and −232 cm^{-1}, respectively. The J value for the iodo derivative must be larger than that of the bromo derivative, since μ_{eff} is independent of T and this large value occurs despite the long Ni–I distance found in the structure.

Reflectance and 1,2-dichloroethane solution spectra of the two compounds show very similar features in each case (Table V). The electronic spectrum of the bromo derivative has a band at 1.00 μm^{-1} and a shoulder at 1.32 μm^{-1}, while that of the iodo derivative has a band at 1.31 μm^{-1}. Both complexes show also intense bands above 1.80 μm^{-1} attributable to

Table V. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd	State[a]	Absorption max, μm^{-1} (ϵ_M for soln)
$[Ni_2Br(nas_3)_2]BPh_4 \cdot 3THF$	a	1.00, 1.31
	a′	0.89 sh, 1.05, 1.43 sh, 1.85 sh
	b	0.91 sh, 1.08 (850)
$[Ni_2I(nas_3)_2]BPh_4 \cdot 3THF$	a	1.31
	a′	1.31, 1.81 sh
	b	1.35 (900), 1.81 sh, 2.10 (1800)

[a] Key: a, diffuse-reflectance spectrum at room temperature; a′, diffuse-reflectance spectrum at ca. 110 K; b, 1,2-dichloroethane solution.

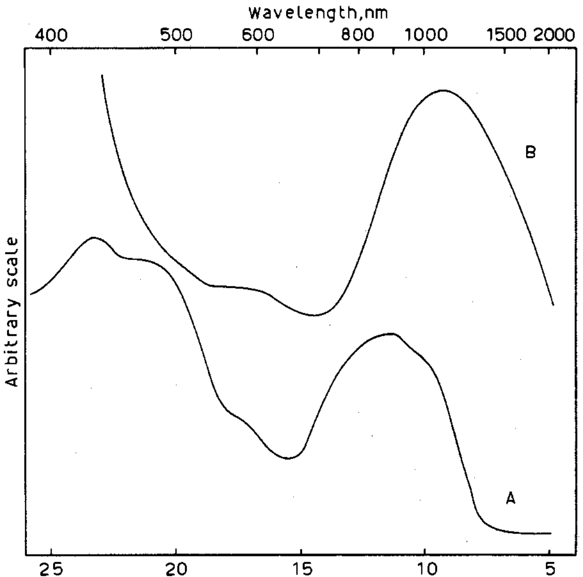

Figure 3. Reflectance spectra of $[Ni_2I(nas_3)_2]BPh_4$ at ca. 110 K (A) and of $NiI(nas_3)$ (B).

charge-transfer transitions. The shape and position of the first band are similar to those of typical five-coordinate nickel(I) complexes such as $NiX(nas_3)$[2] and $NiX(np_3)$[23] which have μ_{eff} = ca. 2 μ_B (Figure 3). The similarity of the low-energy bands to those of d^9 metal complexes which are fully paramagnetic signifies that spin–spin coupling in dinuclear compounds (ca. a few hundred reciprocal centimeters) is small if compared to the d–d transitions (ca. 11 000 cm^{-1}).

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Registry No. $[Ni_2Br(nas_3)_2]BPh_4 \cdot 3THF$, 61091-27-8; $[Ni_2I(nas_3)_2]BPh_4 \cdot 3THF$, 57395-38-7; $[NiBr(nas_3)]BPh_4$, 15051-12-4; $[NiI(nas_3)]BPh_4$, 15051-13-5.

Supplementary Material Available: Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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