of one such progression in the a_1 Mn-S stretch is resolved slightly above the 23,700-cm^{-1} peak.

The $^6A_1 \rightarrow {}^4E(^4D)$ band peaks at 25,477 cm^{-1}. It is well separated from the two observed components of the $^6A_1 \rightarrow {}^4T_1(^4P)$ transition, which fall at 28,011 and 28,329 cm^{-1}. No additional structure in the $^6A_1 \rightarrow {}^4T_1(^4P)$ system is resolved in the 5°K spectrum.

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Registry No. $Mn(SPPh_2NPPh_2S)_2$, 40362-04-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$7.00 for photocopy or \$2.00 for microfiche, referring to the code number INORG-74-1185.

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Metal Complexes as Ligands. IV.[1] Structures of Bis[bis(triphenylphosphine)silver(I)] Bis(1,2-dicyano-1,2-ethylenedithiolato)nickelate(II), $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C_2(CN)_2)_2$, and of Bis[bis(triphenylphosphine)silver(I)] Bis(1,1-dicyano-2,2-ethylenedithiolato)nickelate(II), $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C{=}C(CN)_2)_2$

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Bis[bis(triphenylphosphine)silver(I)] bis(1,2-dicyano-1,2-ethylenedithiolato)nickelate(II), $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C_2(CN)_2)_2$ (A), crystallizes in the monoclinic space group $P2_1/a$ with two molecules per unit cell. The cell dimensions are $a = 22.581$ (28) Å, $b = 13.015$ (12) Å, $c = 14.352$ (14) Å, and $\beta = 119.51$ (1)°. Bis[bis(triphenylphosphine)silver(I)] bis(1,1-dicyano-2,2-ethylenedithiolato)nickelate(II), $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C{=}C(CN)_2)_2$ (B), crystallizes in the monoclinic space group $P2_1/a$ with four molecules per unit cell. The cell dimensions are $a = 26.534$ (12) Å, $b = 12.671$ (7) Å, $c = 22.887$ (10) Å, and $\beta = 105.03$ (1)°. Intensity data for both A and B were collected with a four-circle computer-controlled diffractometer using the θ-2θ scan technique. All 48 nonhydrogen atoms in A were refined anisotropically and the 30 hydrogen atoms were included as fixed atoms. All of the 88 nonhydrogen atoms in B were refined anisotropically. Refinement by block-diagonal matrix least squares using 2124 reflections for A and 3885 reflections for B gave final R factors of 0.041 and 0.063, respectively. The geometry of the NiS_4 group in both structures is square. The interaction of the $Ag(PPh_3)_2^+$ cations in both A and B occurs at the NiS_4 moiety and the silver atoms are located above and below the NiS_4 planes in a chair configuration. Average values of selected bond distances and bond angles in the $(AgP_2)_2NiS_4$ groups are as follows: for A, Ag-Ni, 3.010 Å; Ag-S, 2.780 Å; Ni-S, 2.181 Å; Ag-P, 2.484 Å; Ni-Ag-S, 44.0°; S-Ni-S (interligand), 88.1°; S-Ni-S (intraligand) 91.8°; P-Ag-P, 118.5°. For B, Ag-Ni, 2.936 Å; Ag-S, 2.797 Å (range 2.689-2.916 Å); Ni-S, 2.217 Å (range 2.212-2.224 Å); Ag-P 2.480 Å (range 2.451-2.519 Å); Ni-Ag-S, 45.4° (range 44.2-46.0°); S-Ni-S (interligand), 100.5°; S-Ni-S (intraligand), 79.5°; P-Ag-P, 119.5°.

Introduction

The substitution of the inert counterions that accompany certain ionic chelates, by coordinately unsaturated charged Lewis acids, has proved to be a satisfactory approach to the synthesis of coordination oligomers.[1,3] The specific acid-base interactions observed in these oligomers depend primarily on (a) the availability of basic sites within the ionic chelate and (b) the intrinsic affinities of the metal ions involved for these sites. The effects of these interactions can be studied in the perturbed electronic and structural properties of either the complex acid or the complex base. An acid-base system of this type which we have studied in considerable detail deals with the $M(PPh_3)_2^+$ (M = Ag(I), Cu(I)) adducts of a series of anionic 1,1- and 1,2-dithiolate complexes of nickel(II).[4] In an attempt to establish the nature of the complex acid-complex base interactions for some of these adducts we have determined the solid-state structures of the $[Ag(PPh_3)_2]_2Ni(mnt)_2$ and $[Ag(PPh_3)_2]_2Ni(i\text{-}mnt)_2$ complexes.[5]

Experimental Section

X-Ray Diffraction Measurements. Collection and Reduction of Data. Specific details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I. For each one of the structures, a set of unit cell parameters was derived from the observed diffractometer settings χ, ϕ, and 2θ for three independent reflections. These were refined by a least-squares technique to give the best fit between calculated and observed settings χ, ϕ, and 2θ for 12 independent reflections carefully centered on the diffractometer. The results are shown in Table I.

Intensity data for all structures were obtained by the moving crystal-moving counter technique on an automated diffractometer. A scan speed of 1°/min 2θ was used and the background for each reflection was determined by 10-sec counts at either end of the scan range. At regular intervals (*i.e.*, 40-100 reflections) three "standard"

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[1] Part III: D. Coucouvanis and D. Piltingsrud, *J. Amer. Chem. Soc.*, **95**, 5556 (1973).

[2] Alfred P. Sloan Fellow, 1972-1974.

[3] D. Coucouvanis, N. C. Baenziger, and S. H. Johnson, *J. Amer. Chem. Soc.*, **95**, 3875 (1973).

[4] M. L. Caffery and D. Coucouvanis, paper in preparation.

[5] The following abbreviations will be used throughout the text: mnt, 1,2-dicyano-1,2-ethylenedithiolate; *i*-mnt, 1,1-dicyano-2,2-ethylenedithiolate; PPh_3, triphenylphosphine.

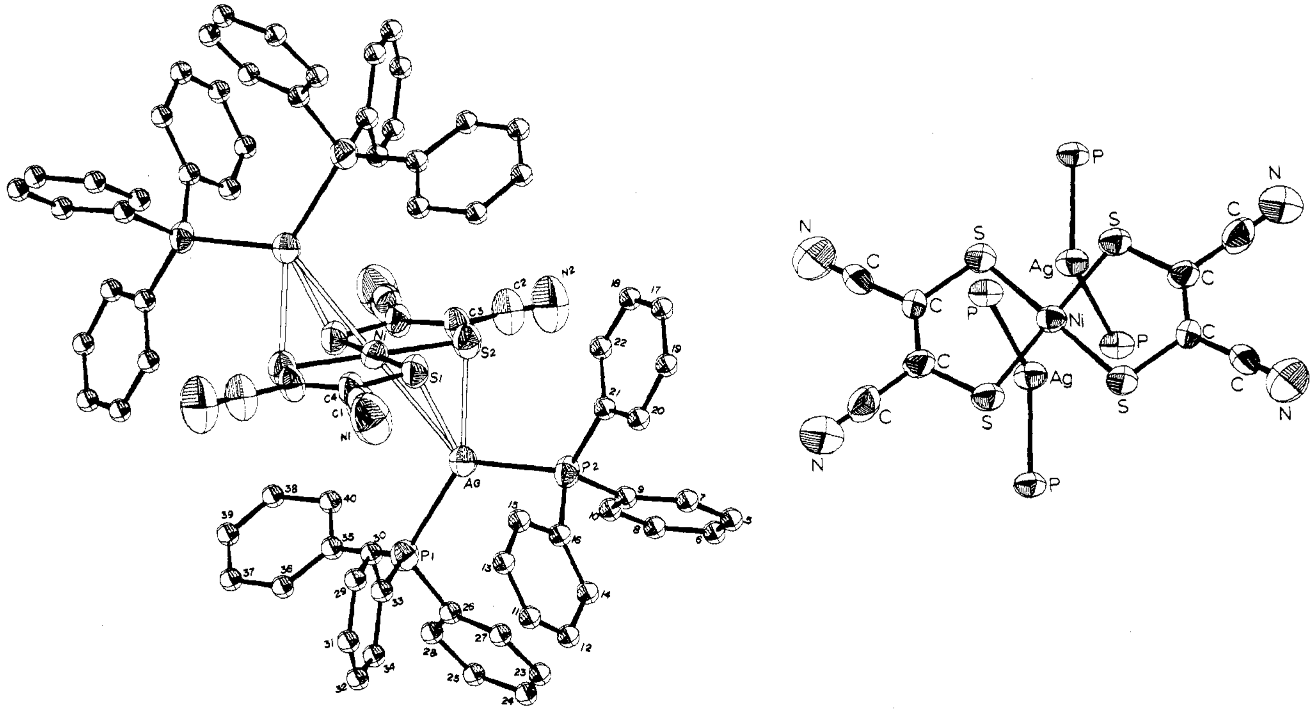

Figure 1. The structure of $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C_2(CN)_2)_2$. Thermal vibrational ellipsoids are scaled to enclose 50% probability. In this and subsequent figures the carbon atoms of the phenyl rings have been assigned artificial isotropic temperature factors of 4 Å^2 for clarity.

Table I. Crystal Intensity Measurement and Structure Determination Data for the $Ag_2NiS_4P_4N_4C_{80}H_{60}$ Complexes

	$Ni(mnt)_2[Ag(PPh_3)_2]_2$[a]	$Ni(i\text{-}mnt)_2[Ag(PPh_3)_2]_2$[a]
Mol wt	1608.4	1608.4
a, Å	22.581 (28)	26.534 (12)
b, Å	13.015 (12)	12.671 (7)
c, Å	14.352 (14)	22.887 (10)
β, deg	119.51 (9)	105.03 (7)
d(obsd),[b] g cm^{-3}	1.43	1.42
d(calcd), g cm^{-3}	1.45	1.44
Z	2	4
Space group[c]	$P2_1/a$	$P2_1/a$
λ(Mo Kα),[d] Å	0.7107	0.7107
μ, cm^{-1}	10.0	10.0
Crystal dimensions, mm	0.56 × 0.34 × 0.29	0.41 × 0.29 × 0.23
Reflections measured	7723	6131
Takeoff angle, deg	3.5	4.0
2θ range, deg	$0 < 2\theta < 40$	$0 < 2\theta < 75°$
Scan width,[e] deg	1.30	1.20
Unique reflections	3413	4823
Atoms in asymmetric unit	48 (+30H)	95
Final R_1	0.041	0.063
Final R_2	0.057	0.073
Reflections used in refinement	2124	3885
No. of parameters	430	856
SDOUW[f]	0.9	2.59

[a] mnt = $(SC(CN))_2{}^{2-}$; *i*-mnt = $(S_2C{=}C(CN)_2)^{2-}$. [b] Determined by flotation in a CS_2–CBr_4 mixture. [c] Systematic absences: *h*0*l* for $h \neq 2n$ and 0*k*0. [d] A graphite single-crystal monochromator was used. [e] A 2θ scan data collection procedure was used. [f] Standard deviation of a reflection of unit weight.

reflections were measured in order to monitor the data collection. No change in crystal quality or instrument performance was detected in any of the structural determinations.

The observed intensities were corrected for background, Lorentz, and polarization effects.[6] Scattering factors for the zerovalent atoms were obtained from ref 7. Where appropriate the calculated structure factors were corrected for the effects of anomalous dispersion[8] of the silver, nickel, sulfur, and phosphorus atoms.[9]

Table II. Reflections Used in Symbolic Addition Procedure[a]

h	*k*	*l*	*E*	Sign
		A.	$Ni(mnt)_2(Ag(PPh_3)_2)_2$	
7	4	8	2.495	+
6	5	8	2.395	+ (to determine origin)
6	6	3	2.304	+
10	1	−1	2.163	−
1	4	−9	2.209	+ (to determine origin)
1	9	−4	2.238	+ (to determine origin)
		B.	$Ni(i\text{-}mnt)_2(Ag(PPh_3)_2)_2$	
6	9	−2	2.538	+ (to determine origin)
14	0	−5	3.5990	+
8	9	7	3.3860	+ (to determine origin)
9	4	3	3.1580	−
11	5	2	3.0250	−
3	5	7	2.9280	+ (to determine origin)

[a] The listed reflections were assigned letter symbols and were used to initiate the symbolic addition procedure. The relationships among these reflections gave rise to the lowest set of contradictions when the listed sign combination was employed.

The standard deviations in the integrated intensities were computed in two ways: (a) from counting statistics

$$\sigma_I = \left(\frac{\Sigma I + \Sigma B}{n}\right)^{1/2}$$

where *I* is the total count in the 2θ scan, *B* is the total background count adjusted for scan time, and *n* is the number of equivalent re-

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(6) (a) Lorentz and polarization corrections, electron density calculations, and full-matrix as well as block-diagonal least-squares calculations were carried out on an IBM 360-65 computer using programs written by Professor N. C. Baenziger of the University of Iowa. Computer drawings were obtained using Johnson's ORTEP thermal ellipsoid plotting program.[6b] In the block-diagonal least-squares calculations 4 × 4 and 9 × 9 blocks were used for isotropic and anisotropic refinement, respectively. (b) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(7) "International Tables for X-Ray Crystallography," Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1965, pp 202, 204.

(8) See ref 7, p 213.

(9) No absorption correction has been applied to either of the two data sets. The value of the linear absorption coefficient is shown in Table I.

Table III. Final Positional[a] and Thermal Parameters[b] for the Atoms in $Ni(mnt)_2[Ag(PPh_3)_2]_2$

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Ag	4178 (1)	3317 (1)	−1532 (1)	33 (1)	49 (1)	48 (1)	−1 (1)	15 (1)	−10 (1)
Ni	5000 (0)	5000 (0)	0 (0)	36 (1)	41 (1)	41 (1)	1 (1)	15 (1)	−7 (1)
S(1)	4210 (2)	5434 (3)	−1612 (3)	39 (2)	52 (3)	50 (2)	−6 (2)	17 (2)	−7 (2)
S(2)	4209 (2)	4293 (3)	229 (3)	36 (2)	74 (3)	40 (2)	−6 (2)	16 (2)	0 (2)
P(1)	4994 (2)	2271 (3)	−1797 (3)	32 (2)	49 (3)	49 (3)	4 (2)	12 (2)	−5 (2)
P(2)	2932 (2)	3025 (2)	−2749 (3)	30 (2)	35 (3)	51 (2)	−2 (2)	13 (2)	1 (2)
N(1)	4010 (5)	6631 (11)	−4115 (8)	68 (8)	168 (14)	70 (8)	14 (11)	29 (7)	22 (11)
N(2)	6025 (5)	7134 (11)	−2261 (9)	65 (8)	180 (16)	88 (10)	−30 (10)	40 (8)	25 (10)
C(1)	4297 (6)	6377 (9)	−3238 (9)	73 (10)	55 (11)	57 (9)	−12 (8)	40 (8)	2 (8)
C(2)	5723 (5)	6719 (11)	−1964 (9)	33 (8)	82 (11)	52 (9)	2 (9)	17 (7)	27 (9)
C(3)	5371 (5)	6196 (9)	−1515 (8)	30 (7)	61 (10)	38 (8)	−7 (7)	10 (6)	11 (8)
C(4)	4677 (5)	6028 (9)	−2126 (8)	59 (9)	50 (9)	30 (8)	−9 (8)	24 (7)	−7 (7)
C(5)	2153 (6)	80 (12)	−1908 (12)	44 (10)	95 (15)	154 (15)	−1 (11)	27 (10)	41 (13)
C(6)	1700 (6)	710 (11)	−2719 (10)	46 (9)	88 (13)	68 (10)	0 (9)	12 (8)	5 (10)
C(7)	2816 (7)	338 (13)	−1395 (12)	92 (13)	118 (17)	133 (15)	0 (12)	26 (12)	79 (13)
C(8)	1915 (6)	1630 (11)	−3019 (9)	46 (9)	58 (11)	76 (10)	−14 (9)	21 (8)	−13 (9)
C(9)	3050 (6)	1219 (11)	−1648 (10)	52 (10)	101 (14)	80 (11)	−4 (9)	11 (9)	20 (10)
C(10)	2609 (5)	1865 (9)	−2471 (8)	37 (8)	63 (10)	48 (8)	−21 (8)	12 (7)	−5 (8)
C(11)	2843 (7)	2831 (12)	−5968 (10)	85 (11)	140 (16)	50 (10)	−32 (12)	20 (9)	7 (11)
C(12)	2667 (7)	1977 (12)	−5699 (10)	84 (11)	115 (16)	69 (10)	−29 (10)	53 (9)	−34 (9)
C(13)	3021 (7)	3706 (13)	−5418 (11)	94 (13)	120 (18)	101 (13)	−22 (12)	36 (11)	12 (12)
C(14)	2633 (6)	1952 (11)	−4710 (10)	69 (11)	88 (13)	88 (11)	−21 (10)	31 (9)	−51 (10)
C(15)	3006 (7)	3693 (13)	−4470 (9)	100 (12)	155 (19)	21 (9)	8 (12)	29 (8)	5 (9)
C(16)	2828 (5)	2838 (10)	−4093 (8)	40 (8)	113 (14)	27 (8)	14 (8)	19 (7)	24 (8)
C(17)	1328 (7)	5418 (11)	−3090 (12)	97 (13)	58 (12)	128 (14)	−9 (10)	48 (12)	−38 (11)
C(18)	1868 (6)	5245 (11)	−2144 (11)	63 (11)	84 (15)	115 (13)	−5 (10)	41 (10)	−31 (10)
C(19)	1239 (6)	4950 (11)	−3987 (11)	49 (8)	67 (11)	112 (12)	34 (10)	12 (9)	35 (11)
C(20)	1712 (7)	4195 (12)	−3955 (10)	77 (11)	93 (15)	54 (10)	26 (10)	2 (9)	21 (9)
C(21)	2281 (5)	4001 (8)	−2955 (8)	43 (8)	26 (7)	56 (9)	−6 (7)	37 (7)	8 (7)
C(22)	2353 (6)	4527 (10)	−2040 (10)	65 (10)	59 (10)	75 (10)	6 (9)	33 (9)	−21 (9)
C(23)	3967 (7)	−385 (12)	−2850 (11)	90 (12)	104 (16)	99 (12)	−25 (12)	33 (10)	1 (11)
C(24)	4393 (9)	−1129 (11)	−2111 (12)	172 (17)	45 (12)	121 (14)	−24 (12)	58 (13)	−7 (11)
C(25)	5009 (9)	−823 (13)	−1353 (14)	140 (7)	73 (16)	176 (19)	16 (14)	−30 (15)	3 (14)
C(26)	4785 (6)	902 (9)	−1923 (9)	41 (8)	47 (10)	69 (10)	−21 (8)	21 (8)	−41 (8)
C(27)	4185 (7)	606 (11)	−2741 (11)	117 (14)	31 (10)	121 (13)	−29 (10)	40 (12)	−7 (10)
C(28)	5245 (7)	219 (13)	−1229 (12)	97 (14)	87 (16)	134 (16)	−24 (11)	−32 (12)	−7 (13)
C(29)	4719 (7)	3967 (12)	−4355 (11)	87 (12)	108 (14)	103 (14)	30 (11)	62 (11)	18 (11)
C(30)	4778 (7)	3656 (10)	−3381 (10)	104 (12)	67 (12)	68 (10)	34 (9)	53 (10)	27 (9)
C(31)	4849 (7)	3292 (12)	−4953 (11)	105 (13)	82 (12)	89 (10)	1 (11)	66 (10)	17 (11)
C(32)	5013 (7)	2314 (12)	−4646 (10)	97 (11)	108 (15)	69 (10)	−30 (11)	53 (9)	−19 (10)
C(33)	4939 (5)	2663 (10)	−3064 (8)	39 (7)	64 (9)	34 (8)	−8 (7)	14 (6)	−1 (7)
C(34)	5075 (7)	1956 (11)	−3683 (10)	106 (13)	79 (13)	68 (11)	−16 (11)	45 (10)	−11 (9)
C(35)	5904 (5)	2367 (9)	−813 (9)	41 (8)	43 (8)	63 (9)	−8 (7)	22 (7)	−25 (8)
C(36)	6421 (6)	2240 (14)	−1041 (10)	46 (10)	217 (21)	72 (11)	34 (12)	40 (9)	24 (12)
C(37)	7092 (6)	2301 (14)	−264 (12)	48 (10)	178 (20)	107 (13)	−3 (12)	24 (10)	16 (13)
C(38)	6773 (7)	2622 (13)	985 (11)	64 (10)	140 (17)	84 (12)	23 (12)	4 (9)	−46 (11)
C(39)	7254 (6)	2474 (11)	759 (11)	28 (9)	84 (13)	128 (14)	−5 (9)	17 (9)	−39 (10)
C(40)	6054 (6)	2527 (11)	226 (10)	58 (10)	114 (14)	72 (10)	25 (10)	28 (9)	−47 (10)

Atom	10^3x	10^3y	10^3z	10^2U	Atom	10^3x	10^3y	10^3z	10^2U
H(5)	201	−56	−169	5	H(25)	530	−139	−87	14
H(6)	121	49	−309	5	H(24)	427	−186	−213	17
H(7)	314	−14	−82	9	H(23)	350	−55	−346	9
H(8)	159	211	−359	5	H(28)	571	46	−69	9
H(9)	355	139	−122	6	H(27)	389	112	−328	12
H(17)	98	591	−313	9	H(40)	568	257	41	6
H(18)	191	565	−152	6	H(38)	696	281	176	7
H(19)	83	517	−466	5	H(39)	774	250	136	3
H(22)	275	438	−131	7	H(36)	631	210	−180	5
H(20)	165	382	−461	8	H(37)	747	222	−44	5
H(11)	284	281	−667	9	H(34)	521	123	−344	10
H(13)	316	432	−569	10	H(32)	509	186	−514	10
H(12)	256	139	−621	8	H(29)	458	469	−463	8
H(14)	248	134	−446	7	H(31)	482	352	−564	10
H(15)	313	434	−403	10	H(30)	470	415	−291	10

[a] In this and the following tables, standard deviations of the least significant figure(s) are given in parentheses. [b] The U values given in this table are defined by the temperature factor expression $\exp[-\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

flections, and (b) from agreement between equivalent reflections if two or more such measurements were made

$$\sigma_I = \left(\frac{\Sigma(I_\mathrm{d} - I_{\mathrm{d_{av}}})^2}{n-1}\right)^{1/2}$$

where $I_\mathrm{d} = I - B$. The largest estimate of the standard deviation was chosen. Experimental weights were used and defined as $w = 1/\sigma_F^2$.

A unique reflection was excluded from the least-squares refinement calculations whenever $I_\mathrm{d} < 3\sigma_B$ (where I_d and B are defined above). In all cases the function minimized was $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$ and the progress of the refinement was judged by the values of the residuals R_1 and R_2.[10]

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(10) $R_1 = \Sigma|\Delta F|/\Sigma|F_\mathrm{o}|$; $R_2 = [\Sigma w(\Delta F)^2/\Sigma w|F_\mathrm{o}|^2]^{1/2}$.

Table IV. Final Positional and Thermal Parameters for the Atoms in Ni(*i*-mnt)$_2$[Ag(PPh$_3$)$_2$][a]

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Ag(1)	2996 (1)	−1401 (1)	2509 (1)	42 (1)	54 (1)	43 (1)	−12 (1)	−12 (1)	10 (1)
Ag(2)	4521 (1)	1920 (1)	2446 (1)	44 (1)	49 (1)	53 (1)	−7 (1)	−19 (1)	5 (1)
Ni	3729 (1)	308 (3)	2519 (1)	82 (2)	87 (3)	77 (2)	−6 (2)	8 (2)	−6 (2)
S(1)	4482 (2)	−196 (4)	2362 (2)	49 (4)	53 (4)	49 (4)	−8 (3)	5 (3)	−9 (3)
S(2)	3449 (2)	−550 (4)	1647 (2)	49 (4)	68 (5)	51 (4)	−3 (3)	0 (3)	−11 (3)
S(3)	2974 (2)	787 (4)	2686 (2)	45 (4)	59 (4)	49 (4)	−5 (3)	3 (3)	−3 (3)
S(4)	4008 (2)	1228 (4)	3363 (2)	45 (4)	71 (5)	52 (4)	2 (3)	1 (3)	−8 (3)
P(1)	5417 (2)	2070 (4)	3126 (2)	35 (4)	55 (5)	47 (4)	0 (3)	−10 (3)	3 (3)
P(2)	4213 (2)	3055 (4)	1558 (2)	45 (4)	63 (5)	43 (4)	2 (3)	−8 (3)	9 (3)
P(3)	2080 (2)	−1699 (4)	1870 (2)	35 (4)	57 (5)	53 (4)	−8 (3)	−3 (3)	3 (3)
P(4)	3295 (2)	−2523 (4)	3411 (2)	48 (4)	57 (5)	44 (4)	−5 (3)	−4 (3)	14 (3)
N(1)	2167 (6)	1883 (20)	3695 (8)	51 (14)	344 (33)	81 (15)	5 (18)	9 (12)	−43 (19)
N(2)	3757 (7)	3002 (15)	4617 (18)	113 (17)	128 (20)	135 (18)	−11 (15)	−63 (14)	−64 (16)
N(3)	5313 (6)	−1121 (17)	1363 (8)	50 (13)	218 (25)	119 (17)	11 (15)	10 (12)	−51 (17)
N(4)	3719 (8)	−1866 (19)	232 (9)	131 (20)	244 (30)	163 (22)	34 (20)	−66 (17)	−125 (21)
C(1)	2578 (7)	1929 (18)	3699 (8)	40 (15)	176 (26)	60 (16)	28 (16)	22 (12)	−12 (17)
C(2)	3128 (7)	1886 (14)	3762 (7)	83 (16)	64 (16)	26 (12)	21 (13)	26 (11)	−25 (12)
C(3)	3351 (6)	1471 (13)	3385 (7)	14 (11)	49 (15)	52 (13)	−1 (10)	−5 (9)	9 (11)
C(4)	3503 (7)	2514 (15)	4242 (9)	58 (16)	72 (18)	99 (18)	26 (13)	22 (13)	11 (14)
C(5)	4888 (7)	−1150 (18)	1324 (8)	44 (15)	168 (26)	79 (17)	0 (16)	25 (13)	−48 (17)
C(6)	4338 (7)	−1108 (16)	1251 (7)	80 (16)	99 (20)	47 (14)	9 (14)	45 (12)	−58 (14)
C(7)	4112 (6)	−769 (13)	1645 (7)	16 (11)	58 (15)	34 (12)	7 (10)	−8 (9)	−8 (11)
C(8)	3957 (8)	−1593 (18)	676 (9)	91 (19)	126 (24)	105 (19)	46 (17)	50 (16)	−23 (18)
C(9)	5527 (7)	3312 (13)	3567 (7)	76 (15)	30 (14)	51 (14)	−10 (12)	21 (12)	−21 (11)
C(10)	4348 (7)	4493 (14)	1750 (7)	116 (18)	38 (16)	39 (14)	−21 (13)	15 (13)	5 (12)
C(11)	3495 (6)	2936 (14)	1222 (8)	25 (13)	61 (17)	71 (15)	14 (12)	−23 (11)	12 (13)
C(12)	4672 (9)	6435 (18)	2116 (10)	133 (22)	97 (23)	124 (22)	−41 (19)	6 (18)	−14 (18)
C(13)	2427 (8)	2732 (16)	685 (9)	97 (19)	78 (20)	90 (18)	12 (15)	24 (15)	30 (15)
C(14)	2619 (7)	2508 (16)	1290 (9)	42 (15)	88 (20)	120 (20)	−8 (13)	−5 (14)	35 (16)
C(15)	2740 (7)	3009 (17)	339 (9)	61 (16)	109 (22)	79 (17)	0 (15)	−13 (13)	14 (16)
C(16)	3172 (7)	2652 (16)	1564 (8)	59 (16)	93 (19)	75 (16)	−9 (14)	35 (13)	19 (14)
C(17)	3305 (7)	3185 (18)	579 (8)	60 (16)	146 (24)	67 (16)	7 (16)	−7 (13)	43 (16)
C(18)	4558 (7)	3599 (18)	525 (8)	61 (16)	152 (24)	66 (16)	−31 (16)	−2 (13)	16 (16)
C(19)	4542 (6)	2779 (15)	946 (8)	18 (12)	93 (18)	52 (14)	−1 (12)	0 (10)	−13 (13)
C(20)	5113 (7)	4026 (15)	3512 (8)	65 (16)	61 (17)	88 (17)	17 (13)	12 (13)	−16 (14)
C(21)	4990 (10)	2282 (19)	68 (11)	114 (21)	157 (27)	104 (20)	−20 (19)	3 (16)	−43 (19)
C(22)	5001 (8)	1508 (21)	464 (10)	94 (20)	183 (29)	104 (21)	14 (20)	11 (16)	−55 (20)
C(23)	5169 (8)	4961 (17)	3846 (9)	113 (20)	87 (20)	79 (18)	14 (16)	−3 (15)	−25 (15)
C(24)	5677 (8)	5154 (16)	4274 (8)	105 (18)	74 (19)	70 (16)	17 (15)	15 (14)	0 (14)
C(25)	6042 (7)	3474 (15)	3994 (8)	55 (15)	84 (18)	52 (14)	−16 (13)	0 (11)	9 (13)
C(26)	6099 (8)	4441 (15)	4330 (8)	122 (20)	46 (17)	59 (15)	−3 (14)	18 (14)	−3 (13)
C(27)	4014 (7)	−2484 (14)	3807 (8)	37 (14)	50 (16)	87 (17)	11 (12)	−5 (12)	−11 (13)
C(28)	1758 (7)	−1126 (16)	2846 (7)	71 (15)	99 (20)	34 (13)	1 (14)	15 (11)	−19 (13)
C(29)	1710 (6)	−622 (12)	1352 (7)	68 (14)	10 (13)	46 (13)	−4 (11)	−5 (11)	−12 (10)
C(30)	2532 (9)	−2599 (18)	4794 (9)	146 (23)	113 (23)	86 (20)	−19 (18)	63 (17)	−27 (17)
C(31)	2458 (9)	−1527 (18)	4879 (9)	159 (23)	103 (22)	57 (17)	−28 (19)	24 (16)	−4 (16)
C(32)	2617 (9)	−771 (2)	4521 (9)	125 (22)	124 (24)	84 (19)	−10 (19)	19 (16)	−20 (17)
C(33)	2959 (6)	−2218 (15)	3977 (7)	42 (14)	104 (19)	30 (13)	5 (13)	15 (11)	−1 (12)
C(34)	2792 (8)	−2927 (17)	4357 (9)	91 (18)	109 (22)	69 (17)	−11 (16)	13 (14)	43 (15)
C(35)	2883 (7)	−1113 (16)	4060 (8)	66 (16)	77 (19)	85 (17)	0 (14)	6 (13)	−19 (15)
C(36)	3114 (7)	−3944 (13)	3203 (7)	119 (18)	15 (14)	27 (12)	−10 (13)	−8 (12)	19 (10)
C(37)	1200 (8)	813 (16)	523 (9)	98 (19)	89 (20)	93 (18)	17 (16)	7 (15)	−6 (16)
C(38)	1467 (7)	−1261 (16)	3285 (9)	71 (17)	96 (20)	86 (18)	−19 (15)	14 (14)	−5 (15)
C(39)	2794 (8)	−5917 (16)	2817 (8)	93 (18)	88 (20)	69 (16)	−31 (15)	−1 (14)	−1 (15)
C(40)	4913 (8)	−1942 (17)	3873 (9)	74 (18)	82 (20)	119 (21)	−28 (15)	0 (15)	−13 (16)
C(41)	4706 (7)	−2912 (17)	4690 (9)	61 (16)	112 (21)	74 (17)	16 (15)	3 (13)	2 (15)
C(42)	4359 (7)	−2018 (15)	3532 (8)	69 (16)	74 (18)	85 (17)	−18 (14)	30 (13)	11 (14)
C(43)	4177 (8)	−3006 (17)	4405 (8)	89 (18)	99 (21)	55 (15)	4 (15)	−12 (13)	27 (15)
C(44)	2399 (10)	−4472 (20)	1076 (10)	165 (26)	132 (27)	124 (23)	57 (21)	−24 (20)	−81 (20)
C(45)	2417 (8)	−5198 (15)	2840 (8)	126 (20)	47 (17)	80 (17)	−15 (15)	7 (15)	−20 (14)
C(46)	2452 (7)	−3580 (16)	1448 (8)	75 (17)	87 (20)	90 (18)	55 (15)	3 (13)	−28 (15)
C(47)	2022 (7)	−2911 (14)	1375 (8)	92 (17)	38 (15)	53 (15)	−19 (13)	0 (12)	−28 (12)
C(48)	3523 (7)	−4670 (16)	3190 (9)	81 (17)	72 (19)	95 (18)	32 (15)	1 (14)	10 (15)
C(49)	2559 (7)	−4173 (16)	3041 (8)	59 (15)	88 (19)	82 (17)	−11 (14)	−23 (13)	27 (15)
C(50)	1909 (8)	−4659 (19)	633 (9)	128 (21)	149 (26)	60 (17)	68 (19)	−18 (15)	−24 (17)
C(51)	1345 (7)	−2801 (15)	2343 (8)	37 (14)	64 (17)	85 (17)	−22 (12)	−6 (12)	19 (13)
C(52)	1497 (8)	−3965 (16)	567 (9)	131 (21)	78 (20)	71 (17)	40 (17)	−28 (15)	−25 (15)
C(53)	1676 (6)	−1906 (14)	2391 (7)	18 (12)	62 (16)	39 (12)	10 (10)	0 (9)	0 (11)
C(54)	3333 (8)	−5683 (16)	2948 (9)	122 (21)	53 (18)	108 (20)	−8 (15)	3 (16)	−13 (15)
C(55)	1537 (7)	−3034 (14)	929 (8)	61 (15)	48 (16)	78 (16)	4 (13)	−27 (12)	−34 (13)
C(56)	1143 (8)	−2108 (17)	3266 (9)	88 (18)	93 (20)	80 (18)	3 (15)	10 (14)	5 (15)
C(57)	1056 (7)	−2899 (16)	2809 (9)	56 (16)	88 (20)	99 (19)	11 (14)	24 (13)	29 (15)
C(58)	5038 (7)	−2448 (15)	4421 (8)	69 (16)	58 (17)	75 (16)	6 (13)	−2 (13)	2 (13)
C(59)	3938 (8)	5204 (17)	1721 (10)	109 (20)	70 (20)	150 (23)	37 (17)	11 (17)	7 (18)
C(60)	4120 (9)	6271 (17)	1922 (11)	147 (24)	47 (19)	198 (29)	20 (17)	37 (21)	12 (19)
C(61)	4748 (7)	1776 (18)	944 (9)	40 (15)	133 (23)	116 (20)	40 (15)	−6 (14)	−41 (17)
C(62)	4803 (8)	3278 (20)	39 (10)	74 (19)	187 (29)	99 (19)	−53 (19)	22 (15)	−13 (20)

Table IV. *(Continued)*

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
C(63)	4908 (7)	4707 (15)	1943 (8)	69 (16)	69 (18)	93 (18)	−33 (14)	−3 (13)	5 (15)
C(64)	947 (9)	458 (20)	949 (11)	131 (23)	125 (26)	162 (26)	50 (20)	−7 (20)	46 (21)
C(65)	1209 (7)	−326 (18)	1395 (10)	49 (16)	119 (23)	142 (22)	59 (16)	−4 (15)	6 (19)
C(66)	1695 (8)	504 (15)	466 (8)	115 (19)	54 (18)	71 (16)	−27 (15)	−17 (14)	3 (14)
C(67)	1980 (7)	−266 (15)	915 (8)	85 (17)	64 (17)	72 (16)	−32 (14)	18 (13)	−7 (14)
C(68)	5437 (7)	965 (16)	4187 (9)	69 (16)	85 (19)	85 (17)	−30 (14)	22 (13)	11 (15)
C(69)	5705 (6)	1010 (14)	3720 (8)	53 (14)	38 (15)	66 (15)	−19 (12)	−6 (11)	−10 (12)
C(70)	5688 (9)	196 (18)	4690 (8)	159 (23)	99 (22)	53 (16)	−73 (19)	−8 (15)	24 (15)
C(71)	5844 (6)	2037 (14)	2607 (7)	36 (13)	63 (16)	36 (12)	36 (11)	9 (10)	28 (11)
C(72)	5793 (7)	1111 (16)	2227 (8)	65 (15)	118 (22)	50 (15)	21 (15)	−3 (12)	−48 (14)
C(73)	6140 (8)	−347 (17)	4590 (10)	88 (19)	87 (21)	150 (23)	6 (16)	−19 (16)	0 (18)
C(74)	6172 (7)	531 (17)	3665 (9)	71 (17)	115 (23)	93 (19)	51 (16)	−36 (14)	6 (16)
C(75)	6381 (9)	−266 (20)	4131 (10)	145 (25)	137 (27)	124 (23)	11 (21)	−2 (19)	2 (20)
C(76)	6102 (7)	1090 (17)	1806 (8)	66 (16)	131 (22)	56 (15)	−4 (16)	18 (12)	−15 (15)
C(77)	6463 (7)	2822 (18)	2123 (9)	55 (16)	142 (24)	80 (18)	−8 (15)	24 (13)	14 (16)
C(78)	6160 (7)	2911 (16)	2569 (8)	32 (14)	122 (21)	55 (14)	−18 (13)	−8 (11)	33 (14)
C(79)	6418 (8)	1928 (17)	1747 (9)	82 (17)	98 (21)	77 (17)	2 (15)	8 (14)	−10 (15)
C(80)	5037 (9)	5702 (17)	2125 (9)	141 (22)	77 (20)	94 (19)	7 (17)	18 (17)	2 (16)

[a] The U values given in this table are defined by the temperature factor expression $\exp[-\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Determination of the Structures

A. $Ni(mnt)_2[Ag(PPh_3)_2]_2$. From the intensity data, corrected for background and Lorentz and polarization effects, the structure was solved by the symbolic addition procedure.[11,12]

The reflections shown in Table II were chosen as starting reflections. An E map was computed using 285 reflections with $E \geqslant 1.50$ and signs obtained from the six starting reflections.

The positions of the nickel (at the center of symmetry) and silver atoms were obtained from the E map and the remaining atoms were located following successive structure factor, Fourier synthesis, and least-squares refinement calculations. Inclusion of all the atoms in a structure factor calculation gave $R_1 = 0.35$. Isotropic temperature factors and the positional parameters of all 48 atoms in the asymmetric unit were refined by a block-diagonal least-squares method to values of 0.075 and 0.088 for R_1 and R_2, respectively. At this point anisotropic temperature factors were assigned to all the noncarbon atoms. Subsequent refinement resulted in values for R_1 and R_2 of 0.059 and 0.075, respectively. Anisotropic temperature factors were then assigned to the carbon atoms and following two cycles of refinement R_1 and R_2 values of 0.048 and 0.065 were obtained. A difference Fourier map now showed several peaks 1.0 e/Å^3 (where the average value for a carbon atom is 6–8 e/Å^3). The positions of all hydrogen atoms were calculated assuming 1.0 Å C–H distances and 120° C–C–H bond angles. Temperature factors equal to the isotropic temperature factors of the carbon atoms adjacent to them were assigned. Two cycles of refinement, where the hydrogen parameters were not refined but were recalculated after each cycle resulted in values for R_1 and R_2 of 0.041 and 0.057, respectively. At this point the refinement was considered complete. All shifts in the last cycle were less than their esd as calculated from the inverse least-squares matrix.

See Figures 1 and 2.

B. $Ni(i\text{-}mnt)_2[Ag(PPh_3)_2]_2$. The intensity data treated as previously described were used to solve the structure by the symbolic addition procedure. An E map was calculated using 342 reflections ($E \geqslant 1.75$) with signs obtained from the six starting reflections (Table II). The positions of the nickel, two silver, and four sulfur atoms were obtained from this map. Subsequent structure factor, Fourier syntheses, difference Fourier syntheses, and least-squares refinement calculations revealed the remaining 88 nonhydrogen atoms. Inclusion of these atoms with isotropic temperature factors in four cycles of block-diagonal least-squares refinement gave values of 0.128 and 0.135 for R_1 and R_2, respectively. At this point anisotropic temperature factors were assigned to all of the 95 atoms in the asymmetric unit and all parameters were refined to final values of 0.063 and 0.073 for R_1 and R_2, respectively. The hydrogen atom positions were calculated as previously described and they were included in the structure factor calculations. No significant improvement was noted however and the hydrogen atoms were not included in the final results. All parameter shifts in the last cycle of least-squares refinement

Table V. Intramolecular Bond Distances and Angles for $Ni(mnt)_2[Ag(PPh_3)_2]_2$[a]

Bond Lengths, Å

Ag–Ni	3.010 (1)	S(2)–C(3)	1.73 (1)
Ag–S(1)	2.760 (3)	C(2)–C(3)	1.42 (1)
Ni–S(1)	2.190 (5)	S(1)–C(4)	1.74 (1)
Ag–S(2)	2.800 (3)	C(1)–C(4)	1.46 (1)
Ni–S(2)	2.173 (3)	C(3)–C(4)	1.39 (1)
S(1)–S(2)	3.033 (5)	P(2)–C(10)	1.81 (1)
Ag–P(1)	2.465 (3)	P(2)–C(16)	1.84 (1)
Ag–P(2)	2.504 (4)	P(2)–C(21)	1.85 (1)
N(1)–C(1)	1.15 (1)	P(1)–C(26)	1.83 (1)
N(2)–C(2)	1.11 (1)	P(1)–C(33)	1.83 (1)
C(1)–C(2)	2.85 (1)	P(1)–C(35)	1.84 (1)

Av[b] phenyl ring C–C distance	1.38 [4]
Av phenyl C–H distance	1.00 [1]

Bond Angles, Deg

Ni–Ag–S(1)	44.4 (1)	Ag–P(2)–C(10)	114.2 (4)
Ni–Ag–S(2)	43.7 (1)	Ag–P(2)–C(16)	105.7 (4)
Ni–Ag–P(1)	106.0 (1)	Ag–P(2)–C(21)	122.5 (4)
Ni–Ag–P(2)	134.2 (1)	C(10)–P(2)–C(16)	105.3 (6)
S(1)–Ag–S(2)	66.1 (1)	C(10)–P(2)–C(21)	103.5 (5)
S(1)–Ag–P(1)	120.6 (1)	C(16)–P(2)–C(21)	104.0 (5)
S(1)–Ag–P(2)	99.5 (1)	N(1)–C(1)–C(4)	178.1 (9)
S(2)–Ag–P(1)	134.5 (1)	C(2)–C(1)–C(4)	58.6 (8)
S(2)–Ag–P(2)	102.6 (1)	N(2)–C(2)–C(3)	176.3 (8)
P(1)–Ag–P(2)	118.5 (1)	C(1)–C(2)–C(3)	60.5 (8)
Ag–Ni–S(1)	61.8 (1)	S(2)–C(3)–C(2)	121.7 (8)
Ag–Ni–S(2)	63.0 (1)	S(2)–C(3)–C(4)	118.0 (8)
S(1)–Ni–S(2)	88.1 (1)	C(2)–C(3)–C(4)	120.0 (7)
Ag–S(1)–Ni	73.9 (1)	S(1)–C(4)–C(1)	116.7 (9)
Ag–S(1)–S(2)	57.6 (1)	S(1)–C(4)–C(3)	122.4 (9)
Ag–S(1)–C(4)	119.7 (3)	C(1)–C(4)–C(3)	120.9 (9)
Ni–S(1)–S(2)	45.7 (1)	P(2)–C(10)–C(8)	121.4 (9)
Ni–S(1)–C(4)	102.4 (4)	P(2)–C(10)–C(9)	119.7 (6)
S(2)–S(1)–C(4)	148.0 (4)	P(2)–C(16)–C(14)	127.9 (9)
Ag–S(2)–Ni	73.2 (1)	P(2)–C(16)–C(15)	113.0 (6)
Ag–S(2)–S(1)	56.3 (1)	P(2)–C(21)–C(20)	122.8 (9)
Ni–S(2)–S(1)	46.2 (2)	P(2)–C(21)–C(22)	117.6 (9)
Ni–S(2)–C(3)	105.1 (4)	P(1)–C(26)–C(27)	117.8 (9)
Ag–P(1)–C(26)	112.2 (4)	P(1)–C(26)–C(28)	119.9 (8)
Ag–P(1)–C(33)	108.0 (3)	P(1)–C(33)–C(30)	118.2 (8)
Ag–P(1)–C(35)	118.8 (4)	P(1)–C(33)–C(34)	120.8 (8)
C(26)–P(1)–C(33)	106.6 (5)	P(1)–C(35)–C(36)	124.8 (8)
C(26)–P(1)–C(35)	106.2 (5)	P(1)–C(35)–C(40)	115.4 (9)
C(33)–P(1)–C(35)	104.2 (5)		

Av phenyl ring C–C–C Angle	120 [3]
Av phenyl ring–H angle	120 [3]

[a] See paragraph at end of paper regarding supplementary material.
[b] In this and following tables, the quantity in brackets following an average value is given by the expression $s = [\Sigma\Delta d^2/(n-1)]^{1/2}$, where Δd is the difference between an individual quantity and the mean value for that quantity.

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(11) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
(12) R. B. K. Dewar, Ph.D. Thesis, 1968, University of Chicago.

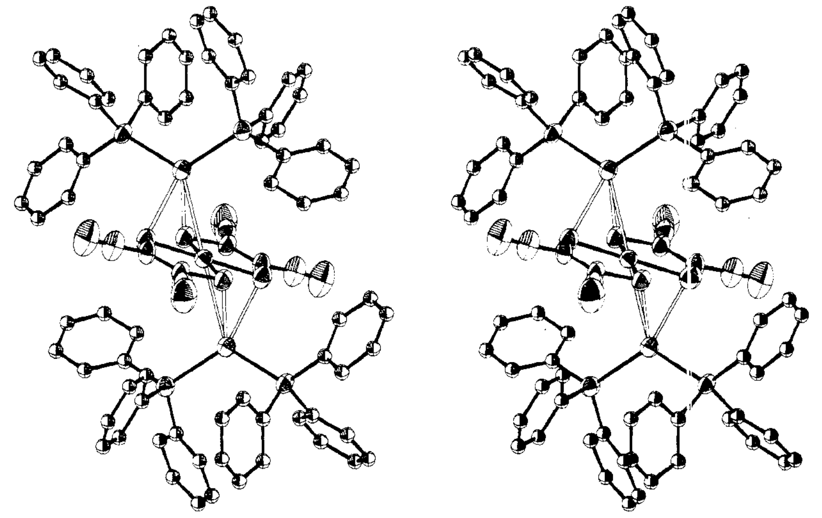

Figure 2. A stereoscopic view of $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C_2(CN)_2)_2$.

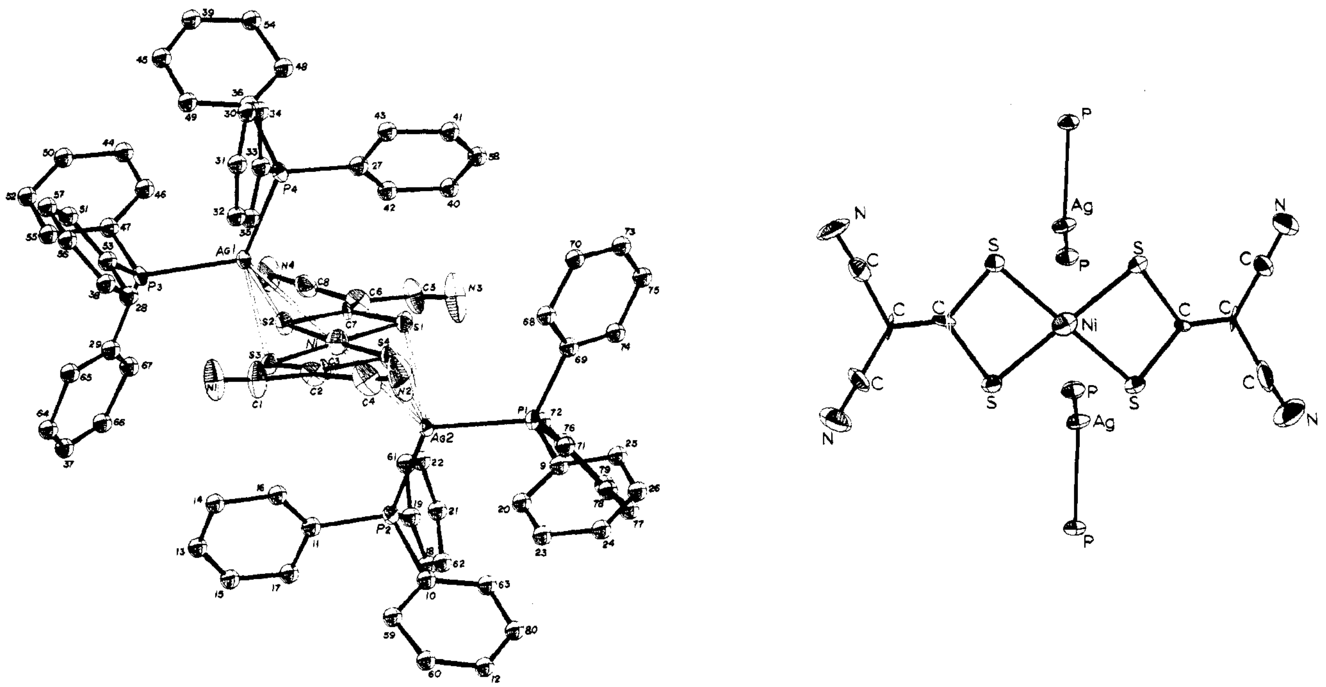

Figure 3. The structure of $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C{=}C(CN)_2)_2$. Thermal vibrational ellipsoids are scaled to enclose 50% probability.

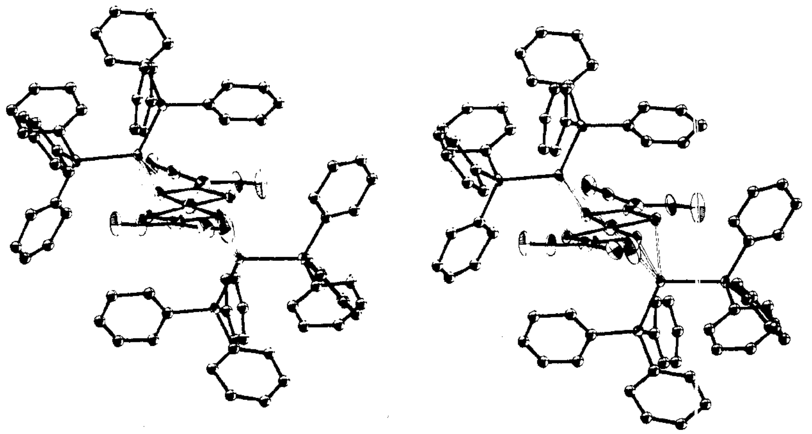

Figure 4. A stereoscopic view of $[Ag(P(C_6H_5)_3)_2]_2Ni(S_2C{=}C(CN)_2)_2$.

Table VI. Intramolecular Bond Distances and Angles for Ni(*i*-mnt)$_2$[Ag(PPh$_3$)$_2$]$_2$ [a]

Bond Lengths, Å

Ag(1)–Ni	2.907 (3)	Ni–S(2)	2.224 (6)	P(1)–C(9)	1.85 (2)	P(4)–C(36)	1.89 (2)
Ag(1)–S(2)	2.780 (5)	Ni–S(3)	2.217 (6)	P(1)–C(69)	1.92 (2)	N(1)–C(1)	1.09 (2)
Ag(1)–S(3)	2.806 (5)	Ni–S(4)	2.212 (6)	P(1)–C(71)	1.84 (2)	N(2)–C(4)	1.13 (3)
Ag(1)–P(3)	2.519 (5)	S(1)–S(2)	2.839 (7)	P(2)–C(10)	1.89 (2)	N(3)–C(5)	1.11 (2)
Ag(1)–P(4)	2.463 (5)	S(1)–S(4)	3.403 (7)	P(2)–C(11)	1.87 (2)	N(4)–C(8)	1.10 (3)
Ag(2)–Ni	2.966 (3)	S(1)–C(7)	1.83 (2)	P(2)–C(19)	1.87 (2)	C(1)–C(2)	1.43 (3)
Ag(2)–S(1)	2.689 (5)	S(2)–S(3)	3.416 (7)	P(3)–C(29)	1.90 (2)	C(2)–C(3)	1.28 (2)
Ag(2)–S(4)	2.916 (5)	S(2)–C(7)	1.78 (2)	P(3)–C(53)	1.82 (2)	C(2)–C(4)	1.51 (3)
Ag(2)–P(1)	2.488 (5)	S(3)–S(4)	2.833 (7)	P(3)–C(47)	1.89 (2)	C(5)–C(6)	1.43 (3)
Ag(2)–P(2)	2.451 (5)	S(3)–C(3)	1.87 (2)	P(4)–C(27)	1.89 (2)	C(6)–C(7)	1.28 (2)
Ni–S(1)	2.215 (6)	S(4)–C(3)	1.78 (2)	P(4)–C(33)	1.79 (2)	C(6)–C(8)	1.56 (3)

Av phenyl ring C–C distance 1.42 [4]

Bond Angles, Deg

Ni–Ag(1)–S(2)	46.0 (1)	Ag(2)–Ni–S(2)	111.3 (2)	Ni–S(2)–C(7)	88.8 (5)	Ag(2)–P(1)–C(71)	104.1 (6)
Ni–Ag(1)–S(3)	45.6 (1)	Ag(2)–Ni–S(3)	120.4 (1)	S(1)–S(2)–S(3)	89.7 (2)	Ag(2)–P(2)–C(10)	111.8 (6)
Ni–Ag(1)–P(3)	131.2 (1)	Ag(2)–Ni–S(4)	66.7 (2)	S(1)–S(2)–C(7)	38.8 (5)	Ag(2)–P(2)–C(11)	112.3 (5)
Ni–Ag(1)–P(4)	110.8 (1)	S(1)–Ni–S(2)	79.5 (2)	S(3)–S(2)–C(7)	128.5 (6)	Ag(2)–P(2)–C(19)	113.1 (5)
S(2)–Ag(1)–S(3)	75.4 (1)	S(1)–Ni–S(3)	178.9 (2)	Ag(1)–S(3)–Ni	65.6 (1)	Ag(1)–P(3)–C(29)	121.2 (5)
S(2)–Ag(1)–P(3)	100.1 (1)	S(1)–Ni–S(4)	100.5 (2)	Ag(1)–S(3)–S(2)	52.0 (2)	Ag(1)–P(3)–C(47)	112.7 (6)
S(2)–Ag(1)–P(4)	135.6 (2)	S(2)–Ni–S(3)	100.5 (2)	Ag(1)–S(3)–S(4)	102.7 (2)	Ag(1)–P(3)–C(53)	106.6 (5)
S(3)–Ag(1)–P(3)	100.3 (2)	S(2)–Ni–S(4)	177.5 (2)	Ag(1)–S(3)–C(3)	123.8 (5)	Ag(1)–P(4)–C(27)	116.9 (6)
S(3)–Ag(1)–P(4)	117.6 (2)	S(3)–Ni–S(4)	79.5 (2)	Ni–S(3)–S(2)	39.8 (2)	Ag(1)–P(4)–C(33)	111.7 (6)
P(3)–Ag(1)–P(4)	116.9 (2)	C(3)–Ni–C(7)	177.9 (5)	Ni–S(3)–S(4)	50.2 (1)	Ag(1)–P(4)–C(36)	109.4 (6)
Ni–Ag(2)–S(1)	45.8 (1)	Ag(2)–S(1)–Ni	73.7 (2)	Ni–S(3)–C(3)	88.2 (5)	N(1)–C(1)–C(2)	173 (2)
Ni–Ag(2)–S(4)	44.2 (1)	Ag(2)–S(1)–S(2)	102.3 (2)	S(2)–S(3)–S(4)	89.9 (2)	C(1)–C(2)–C(3)	126 (1)
Ni–Ag(2)–P(1)	126.5 (1)	Ag(2)–S(1)–S(4)	55.7 (1)	S(2)–S(3)–C(3)	128.0 (5)	C(1)–C(2)–C(4)	121 (2)
Ni–Ag(2)–P(2)	111.2 (1)	Ag(2)–S(1)–C(7)	117.5 (5)	S(4)–S(3)–C(3)	38.0 (5)	C(3)–C(2)–C(4)	112 (1)
S(1)–Ag(2)–S(4)	74.6 (1)	Ni–S(1)–S(2)	50.4 (1)	Ag(2)–S(4)–Ni	69.1 (1)	S(3)–C(3)–S(4)	101.8 (6)
S(1)–Ag(2)–P(1)	97.7 (2)	Ni–S(1)–S(4)	39.7 (2)	Ag(2)–S(4)–S(1)	49.6 (1)	S(3)–C(3)–C(2)	122 (1)
S(1)–Ag(2)–P(2)	121.9 (2)	Ni–S(1)–C(7)	87.8 (5)	Ag(2)–S(4)–S(3)	103.4 (2)	S(4)–C(3)–C(2)	136 (1)
S(4)–Ag(2)–P(1)	97.0 (2)	S(2)–S(1)–S(4)	90.1 (2)	Ag(2)–S(4)–C(3)	127.6 (6)	N(2)–C(4)–C(2)	175 (1)
S(4)–Ag(2)–P(2)	131.0 (2)	S(2)–S(1)–C(7)	37.5 (5)	Ni–S(4)–S(1)	39.8 (2)	N(3)–C(5)–C(6)	175 (1)
P(1)–Ag(2)–P(2)	122.1 (2)	S(4)–S(1)–C(7)	127.4 (5)	Ni–S(4)–S(3)	50.3 (1)	C(5)–C(6)–C(7)	126 (6)
Ag(1)–Ni–Ag(2)	174.2 (1)	Ag(1)–S(2)–Ni	70.0 (1)	Ni–S(4)–C(3)	90.4 (6)	C(5)–C(6)–C(8)	120 (1)
Ag(1)–Ni–S(1)	114.4 (2)	Ag(1)–S(2)–S(1)	100.5 (1)	S(1)–S(4)–S(3)	90.1 (2)	C(7)–C(6)–C(8)	114 (1)
Ag(1)–Ni–S(2)	64.0 (2)	Ag(1)–S(2)–S(3)	52.6 (2)	S(1)–S(4)–C(3)	130.2 (6)	S(1)–C(7)–S(2)	104 (1)
Ag(1)–Ni–S(3)	64.8 (2)	Ag(1)–S(2)–C(7)	123.4 (6)	S(3)–S(4)–C(3)	40.1 (6)	S(1)–C(7)–C(6)	122 (1)
Ag(1)–Ni–S(4)	118.1 (2)	Ni–S(2)–S(1)	50.1 (1)	Ag(2)–P(1)–C(9)	113.4 (5)	S(2)–C(7)–C(6)	134 (1)
Ag(2)–Ni–S(1)	60.5 (2)	Ni–S(2)–S(3)	39.7 (2)	Ag(2)–P(1)–C(69)	121.9 (6)		

Av phenyl ring C–C–C angle 1.20 [4]

[a] See paragraph at end of paper regarding supplementary material.

were less than 0.5 times their esd as calculated from the inverse least-squares matrix.

See Figures 3 and 4.

Crystallographic Results

Atomic positional parameters with standard deviations derived from the inverse matrix of the least-squares refinement are compiled in Tables III and IV for the structures of Ni(mnt)$_2$[Ag(PPh$_3$)$_2$]$_2$ and Ni(*i*-mnt)$_2$[Ag(PPh$_3$)$_2$]$_2$, respectively.[13] Intramolecular bond distances and angles are given in Tables V and VI. The atom-labeling schemes are shown in Figures 1 and 3.

Discussion

The interaction of the Ag(PPh$_3$)$_2^+$ cations with the Ni(mnt)$_2^{2-}$ and Ni(*i*-mnt)$_2^{2-}$ complex anions occurs at the NiS$_4$ moiety. In both structures the silver atoms are located above and below the NiS$_4$ planes in a "chair" configuration and are in close proximity to a triad of atoms defined by two sulfurs and the nickel (Figures 1, 3). A characteristic feature of both structures is that the phosphorus, silver, and nickel atoms lie in a plane which is approximately perpendicular to the plane of the complex anion.

The average values of the Ag-P bond lengths (Tables V, VI) are very similar to the average values of 2.47 (3) Å found[14] in the structures of the M(O$_2$C$_2$S$_2$)$_3$(Ag(PPh$_3$)$_2$)$_3$ complexes (M = Fe(III), Al(III)) and only slightly greater than the sum of the covalent radii of the Ag and P atoms of 1.34 and 1.06 Å, respectively.[15]

The observed Ag-S and Ag-Ni distances (Tables V, VI) are longer than single covalent bonds but appreciably shorter than the van der Waals contacts of 3.52 and 3.35 Å for Ag-S and Ag-Ni, respectively.[16] Some typical Ag-S covalent bond lengths reported in the literature are the average Ag-S distances in silver monothiocarbamate[17] (2.46 (3) Å), silver dithiocarbamate[18] (2.44 (1) Å), silver thiocyanate[19] (2.34 (2) Å), and bis(thiourea)silver chloride[20] (2.43-2.59 Å).

The NiS$_4$ grouping in both structures is essentially planar. Small deviations from planarity are noted however when the complete Ni(mnt)$_2^{2-}$ and Ni(*i*-mnt)$_2^{2-}$ units are considered (Table VII) and probably are due to packing forces. The structural details of the Ni(mnt)$_2^{2-}$ unit (Table V) are within 3σ of those previously reported in other structural determina-

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Table VII. Weighted Least-Squares Planes

Deviations from the Planes (Å) of Atoms Used to Define the Planes and Dihedral Angles between Selected Planes

$Ni(mnt)_2[Ag(PPh_3)_2]_2$					$Ni(\textit{i}\text{-}mnt)_2[Ag(PPh_3)_2]_2$					
Atom	Plane 1	Plane 2	Plane 3	Plane 4	Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Ag	−0.000 (1)		0.000 (2)		Ag(1)	0.041 (2)			0.000 (2)	
Ag′[a]				0.000 (2)	Ag(2)	−0.013 (2)				0.000 (2)
Ni	0.571 (0)	0.032 (0)	0.000 (5)		Ni	−0.134 (3)	−0.02 (1)	−0.008 (3)		
S(1)		−0.037 (4)	0.000 (5)		S(1)		−0.12 (1)	−0.029 (5)		0.000 (5)
S(2)		0.018 (4)		0.000 (5)	S(2)		−0.00 (1)	0.041 (5)	0.000 (5)	
S(1′)				0.000 (5)	S(3)		0.03 (1)	−0.029 (5)	0.000 (5)	
S(2′)					S(4)		0.05 (1)	0.041 (5)		0.000 (5)
N(1)		0.122 (14)			N(1)		−0.28 (2)			
N(2)		−0.009 (14)			N(2)		0.37 (2)			
					N(3)		0.37 (2)			
					N(4)		0.38 (2)			
C(1)		0.061 (13)			C(1)		−0.09 (2)			
C(2)		0.010 (13)			C(2)		−0.03 (2)			
C(3)		0.006 (12)			C(3)		0.06 (2)			
C(4)		0.026 (12)			C(4)		0.21 (2)			
					C(5)		0.24 (2)			
					C(6)		0.18 (2)			
					C(7)		−0.00 (2)			
					C(8)		0.22 (2)			
P(1)	0.000 (4)				P(1)	0.145 (5)				
P(2)	0.000 (3)				P(2)	0.101 (5)				
					P(3)	−0.103 (5)				
					P(4)	−0.120 (5)				

Dihedral Angles, Deg

$Ni(mnt)_2[Ag(PPh_3)_2]_2$		$Ni(\textit{i}\text{-}mnt)_2[Ag(PPh_3)_2]_2$	
Plane 1-plane 2	−75.1	Plane 1-plane 2	−82.3
Plane 2-plane 3	−79.0	Plane 2-plane 4	74.1
Plane 2-plane 4	−79.0	Plane 2-plane 5	72.8
		Plane 4-plane 5	1.5
		Plane 1-plane 4	−85.03
		Plane 1-plane 5	−85.65

[a] Primed atom is related to umprimed atom by 1 − *x*, 1 − *y*, −*z*.

tions of the same complex anion[21-23] and indicate that the perturbation brought about by the $(PPh_3)_2Ag^+$ cation is not sufficient to alter appreciably the electronic structure of the $Ni(mnt)_2^{2-}$ complex. Structural details within the $Ni(\textit{i}\text{-}mnt)_2^{2-}$ complex are similar to those found with other 1,1-dithiolate complexes.[23-25] The P-Ag-P angles of 118.5 (1) and of 116.9 (2) and 122.1 (2) (Tables V, VI) found in the structures of the $Ni(mnt)_2^{2-}$ and $Ni(\textit{i}\text{-}mnt)_2^{2-}$ adducts, respectively, suggest an sp^2-hybridized silver atom. A possible description of the bonding in the adducts would involve overlap between a silver sp^2-hybrid orbital and a localized molecular orbital consisting of sulfur and nickel atomic functions. However, among the factors that are believed to influence the P-Cu-P angle in $(Ph_3P)_2CuX$ complexes are steric effects across the P-Cu-X bonds.[26,27] An examination of the shortest intramolecular and intermolecular contacts in the two structures (Table VIII) shows that the P-Ag-P angle cannot "open up" further without steric hindrance. On the basis of recent studies of the $[(R_3P)_2Ag]_2Ni(mnt)_2$ complexes with sterically less hindered phosphines[28] we have reached the conclusion that steric effects are indeed important in determining the magnitude of the P-Ag-P angle.

Table VIII. Closest Intra- and Intermolecular Contacts (Å)

Intramolecular contacts		Intermolecular contacts	
A. $Ni(mnt)_2[(PPh_3)_2Ag]_2$			
C(13)-C(29)	3.373 (19)	N(1)-C(14)	3.26 (2)
C(13)-C(30)	3.583 (19)	N(1)-C(31)	3.44 (2)
S(1)-C(40)	3.535 (13)	N(2)-H(23)	2.38 (1)
C(18)-C(39)	3.578 (19)	N(2)-C(39)	3.42 (2)
B. $Ni(\textit{i}\text{-}mnt)_2[(PPh_3)_2Ag]_2$			
S(1)-C(42)	3.615 (19)	N(1)-C(78)	3.21 (2)
S(3)-C(16)	3.626 (19)	N(3)-C(51)	3.35 (2)
C(40)-C(70)	3.616 (28)	N(4)-C(13)	3.26 (3)
N(3)-C(72)	3.497 (26)	N(4)-C(37)	3.45 (3)
N(3)-C(76)	3.487 (28)		
C(20)-C(63)	3.595 (27)		
C(72)-C(61)	3.578 (26)		

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Registry No. $[Ag(PPh_3)_2]_2Ni(MNT)_2$, 50860-39-4; $[Ag(PPh_3)_2]_2Ni(\textit{i}\text{-}MNT)_2$, 51014-20-1.

Supplementary Material Available. Continuations of Tables V and VI showing detailed lists of individual phenyl ring C-C and C-H distances and of C-C-C and phenyl ring-H angles for $Ni(mnt)_2[Ag(PPh_3)_2]_2$ and $Ni(\textit{i}\text{-}mnt)_2[Ag(PPh_3)_2]_2$, respectively, and listings of structure factor amplitudes for these compounds will appear follow-

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Quantum Mechanical Description of Electrode Reactions. I. Extended Huckel Molecular Orbital Treatment of the Halide-Bridged Electrode Reactions of Platinum Complexes

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The extended Huckel molecular orbital method has been employed to calculate the activation energies of the halide bridged electrochemical interconversion of typical Pt(IV) and Pt(II) complexes. Conventional spectroscopic values of the mo parameters were employed. When combined with the theory of absolute rates for adiabatic reactions, the calculated activation energies led to theoretical rates in qualitative agreement with experimental values based upon the Tafel equation and the Gouy-Chapman-Stern theory of electrode processes. Covalent interaction between the reactants and the electrode surface, although important in establishing the reaction pathway, was neglected in these calculations and will be introduced at a later stage. The procedure described here appears to allow unequivocal identification of the electronic states primarily responsible for electron-transfer between typical electrodes and reactants and thus may be of considerable practical interest for correlating, interpreting, or predicting the courses of electrode reactions.

Introduction

Electrochemical interconversion of Pt(II) and Pt(IV) is facilitated by halide ions and halogen ligands.[1-5] It appears that in each instance the halogen acts as a bridging group between the Pt ion of the complex and the electrode surface. Comparison of trends in electrode rate[2-5] with spectral energy levels and the results of semiempirical molecular orbital calculations[6] suggests that electron transfer proceeds between an $a_{1g}(\sigma^*)[5d_{z^2}]$ level of the Pt complex and certain appropriate levels of the electrode surface by way of the bridging halide ion or ligand.[5]

Electrolysis results in addition or removal of two ligands along one trans axis (eq 1) (here denoted the *z* axis). According to the Franck-Condon principle the X-Pt-Z internuclear distances must decrease upon approaching the transition state for oxidation of Pt(II) and, conversely, must increase prior to reduction of Pt(IV). Energies of the highest occupied, lowest unoccupied, and nearby orbitals of hexachloroplatinum(II), -(III), and -(IV) calculated by means of the extended Huckel method in terms of this "*z*-axis" internuclear distance, r_z, appear in Figure 1. From Figure 1 it can be seen that the energy of $a_{1g}(\sigma^*)[5d_{z^2}]$ increases sharply as the Pt-Cl distance is decreased while the energies of other orbitals are relatively unaffected, indicating that this is the orbital which is occupied in $Pt^{II}L_4$, unoccupied in *trans*-$Pt^{IV}L_4X_2$, and most strongly involved in the interconversion process.

$$Pt^{II}L_4 + X^- + Z \rightleftharpoons trans\text{-}Pt^{IV}L_4XZ + 2e^- \qquad (1)$$

$$(X^- = Cl^-, Br^-, I^-; Z = X^-, H_2O; L = X^-, Z, NO_2^-, R_3N)$$

Pt(IV)-Pt(II) couples for which L = NR_3 or H_2O are invariably more reactive than those for which L = Cl^-, Br^-, I^-, NO_2^-, CN^-, or SCN^-.[2,5] Coulombic attraction facilitates coordination of $Pt(NR_3)_4^{2+}$ with the adsorbed-halide bridge, X^-, and the trans group, Z, prior to oxidation. This attraction, of course, gives way to repulsion as neutral ligands are replaced by anionic ones. The potential energy surface for $X\cdots[Pt(NR_3)_4]^{2+}\cdots Z$ involves smaller values of the *z*-axis Pt-X internuclear distance, r_z, when Z is a neutral species than when Y is an anion. The variation of potential energy with r_z is less dependent upon the identity of the in-plane ligands, L, for Pt(IV) than for Pt(II) because substantial delocalization of charge over the X-Pt-Z axis occurs. Graphs of free molecule potential energy *vs.* *z*-axis Pt-X internuclear distance for various Pt complexes, calculated by means of the extended Huckel method, appear in Figure 2.

Interactions involving the electrode were not considered in making the calculations displayed in Figure 2. However, a full treatment of the potential energy surface for a model which includes atoms of the electrode will be reported in the near future; the problems of selecting models to represent the metal crystal surface in contact with electrolyte will be described separately.[7]

Factors leading to the ability of various species, notably halides and unsaturated organic compounds, to act as ligand bridges in the homogeneous electron-transfer reactions of transition metal complexes[8] have been discussed qualitatively by Halpern and Orgel.[9] It appears that the homogeneous and heterogeneous cases are analogous,[10] with the electrode

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