corrinoid educt. The observation—surprising at the time—that this complex is thermally stable, and the subsequent finding that cyclization requires prior base-induced deprotonation of a peripheral methylene group, can therefore not be ascribed to stereoelectric factors in the seco-corrinoid educt. The structural results would seem to provide strong support for the alternative hypothesis—that the main function of the base is to increase the nucleophilicity of the exocyclic methylidene carbon C(15).

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9. Crystallographic Studies of Synthetic Corrinoids. III. Structural similarities and differences between A/D-seco-corrinoid complexes of divalent nickel, palladium and platinum

by **Murdoch Currie**[1]) and **J. D. Dunitz**

Laboratorium für organische Chemie der Eidg. Technischen Hochschule, 8006 Zürich

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Summary. X-ray crystal structure investigations of the isomorphous perchlorate salts of complexes of an A/D-seco-corrinoid ligand (I) with divalent nickel, palladium and platinum are reported. The structures determined for the Pd- and Pt-complexes are virtually superposable, that of the Ni-complex, although similar to the other two, shows significant differences with respect to metal coordination and to the spatial relationship of the A and D rings and their substituents. These similarities and differences are discussed in relation to the photochemical A/D cyclization leading to corrin complexes (II).

The synthesis of corrin compounds (II) by A/D ring closure of seco-corrins (I) devised, accomplished and investigated by *Eschenmoser* and co-workers [1] has led to a number of unexpected results concerning the rôle of the central metal atom. Initially, this rôle was presumed to be limited to imposing the necessary geometric restrictions on the seco-corrinoid ligand. If the ligand could be made to form a coil in which one of the hydrogen atoms of the α-methylene group of ring D was exactly above or below the exocyclic double bond and in reasonable proximity to it, then the geometric conditions for an antarafacial 1,16-hydrogen shift would be approximately fulfilled. From orbital-symmetry considerations, such a shift should be forbidden

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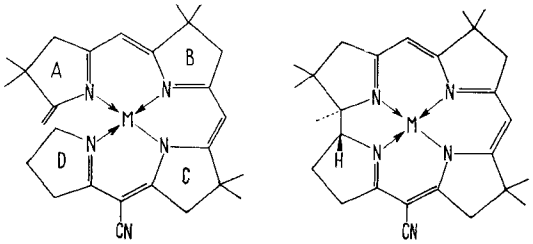
[1]) Present address: Chemistry Department, University of Glasgow, Glasgow W. 2, Scotland.



I II

thermally but allowed photochemically. The new conjugated 15-centre 16-electron π-system so produced contains 2 electrons in a formally non-bonding molecular orbital and would be expected to undergo an antarafacial A/D cyclization to give the product II. From model considerations it seemed likely that the necessary geometric restrictions on the seco-corrin ligand would be imposed by square-planoid coordination of the 4 nitrogen atoms about a central metal atom. The Ni^{II}-complex proved to be completely resistant to cyclization, both thermally and photochemically; the Pd^{II}-complex, on the other hand, undergoes photochemical cyclization to II very readily and in essentially quantitative yield. It was first thought that this difference in the chemical behaviour of the Ni^{II}- and Pd^{II}-complexes might be connected with the stronger tendency of the latter towards square-planar coordination. However, complexes with Zn^{II}, Mg^{II} and Cd^{II} have recently been shown to cyclize even more readily than the Pd^{II}-complex [2]. Moreover, the corresponding complex with Pt^{II}, which has, if anything, an even stronger tendency towards square-planar coordination than Pd^{II}, undergoes cyclization less readily than the Pd^{II}-complex. These differences in chemical behaviour make it seem very likely that the rôle of the central metal is not limited to the mere imposition of suitable geometric restrictions on the seco-corrinoid ligand, but that interactions between electrons on the metal and those on the ligand influence the ease of cyclization in some as yet not understood way [1]. The full story, when it is finally unravelled, is likely to be rather intricate.

One contribution to the understanding of the rôle of the metal atoms in this and other photochemically active systems would be the determination of the actual spatial relationships between the reacting centres in these structurally similar yet chemically different complexes. As a first step in this direction, we have carried out crystal structure analyses on the series of isomorphous perchlorate salts of the seco-corrinoid complexes I with Ni^{II}, Pd^{II} and Pt^{II}. Our results, described in detail in the remainder of this paper, show that in all three complexes the actual stereoelectronic relationships are, as far as can be judged, almost ideal for the cyclization. Nevertheless, there are small differences between the Ni^{II}-complex on the one hand and the Pd^{II}- and Pt^{II}-complexes on the other, that must be relevant to the differences in ease of cyclization and may possibly be decisive.

Crystallographic data. – Well formed crystals of all three compounds as perchlorate salts ($C_{27}H_{34}N_5MClO_4$, M = Ni, Pd, Pt) were provided by Dr. *Y. Yamada* and Mr. *H. Wild*. The Ni-complex had been recrystallized from methyl acetate, the Pd- and Pt-complexes from acetone. The three compounds form an isomorphous series, with crystallographic data as follows:

	Ni-complex	Pd-complex	Pt-complex
Molecular weight	568.8	634.5	723.6
a (Å)	10.294	9.911	9.889
b (Å)	11.591	11.738	11.738
c (Å)	14.069	14.246	14.238
α (°)	111.374	111.396	111.368
β (°)	102.490	101.960	102.130
γ (°)	93.486	94.681	94.732
Space group (assumed)	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
V (Å^3)	1508	1487	1482
D_m	1.36	1.45	1.67
D_x ($Z = 2$)	1.292	1.417	1.621
μ (Mo$K\alpha$)	7.71	7.45	51.13

All three crystals contain small, variable amounts of occluded solvent (methyl acetate for the Ni-complex, acetone for the Pd- and Pt-complexes), as suggested by the discrepancies between observed and calculated densities.

During the subsequent analysis of the *Ni-complex* the presence of solvent was confirmed by the appearance of an otherwise inexplicable, diffuse, elongated electron-density peak in the intermolecular cavity centred at $(x, y, z) = (^1/_2, ^1/_2, 0)$. The maximum peak height was approximately 2.5 e/Å^3 and integration of the peak gave a count of about 28 electrons, corresponding to about 70% occupation of the cavity by CH_3COOCH_3, which must be statistically distributed over at least four orientations to account for the observed peak shape. The observed density corresponds to the presence of approximately 0.8 mol. of CH_3COOCH_3 per unit cell, but chemical analysis (C/H/N) gave a composition corresponding to only 0.4 mol. per unit cell. The differences between these estimates may be ascribed partially to the inaccuracies inherent in the methods and probably also to variations in the actual amount of solvent in different crystal specimens and under different experimental conditions. At any rate, the solvent does not seem to be present in stoichiometric amounts.

For the *Pd-complex*, an electron-density peak centred at $(^1/_2, ^1/_2, 0)$ and containing approximately 20 electrons, corresponding to about 0.6 mol. of CH_3COCH_3 per unit cell, was also found in the difference synthesis. The corresponding estimates are 0.5 mol. from the observed density and 0.8 mol. from C/H/N analysis.

For the *Pt-complex*, no electron-density or difference synthesis has been calculated, but it seems likely that the crystals are also partially solvated.

Intensity measurements. – Intensity measurements for all three crystals were made with a *Hilger & Watts* Y 290 four-circle diffractometer controlled by a PDP8 computer. However, each crystal was measured under somewhat different conditions as follows:

	Ni-complex	Pd-complex	Pt-complex
Crystal dimensions (mm)	0.35 × 0.25 × 0.10	0.22 × 0.18 × 0.10	0.44 × 0.16 × 0.06
Radiation Mo$K\alpha$	– Sr/Zr balanced filters –		monochromated
Source collimator diameter (mm)	1.0	0.5	–
Diffracted beam collimator diameter (mm)	2.0	3.5	3.5
Background count (sec.)	2 × 22.5	2 × 15	2 × 18.75
Scan, no. of points, interval	$\omega/2\theta$ (60, 0.01°)	ω(40, 0.02°)	ω(50, 0.02°)
Measuring time per Point (sec.)	1.5	1.5	1.5
Total measurement time per reflexion (sec.)	2 × 135	2 × 90	112.5
Θ-range I	0–20°	0–21°	0–25°
Θ-range II	20–25°	21–25°	25–28°
Independent reflexions measured	3079	3312	6056

A measurement was carried out for every independent reflexion in Θ-range I, whilst in Θ-range II measurements were carried out only for the stronger reflexions, which were selected on the basis of a 'quick scan' (10 points at 0.01° interval, 1 sec. measuring time per point). The standard deviation of a net integrated intensity I was taken to be given by the expression $[(P_{Zr}+P_{Sr})+K(B_{Zr}+B_{Sr})]^{1/2}+0.03\,I$ where P_{Zr}, P_{Sr}, B_{Zr}, B_{Sr} are peak and background counts for Zr and Sr filters respectively, and K is a constant to allow for the ratio of peak: background measurement times.

Structure analysis and refinement. – The Ni-complex was available first. Approximate positions for all non-hydrogen atoms in this complex were derived by straightforward application of the heavy-atom method and used as a basis for the refinement of all three structures by full-matrix least-squares analysis. In the earlier least-squares cycles the vibrational parameters were regarded as isotropic (isotropic cycles). In later cycles (for the Ni- and Pd-complexes) the vibrational parameters of the metal, chlorine and oxygen atoms were regarded as anisotropic (anisotropic cycles); since the anisotropic cycles had to be split into two parts, each involving 19 atoms, because of computer-storage limitations, cross-terms between pairs of atoms in the different parts are neglected.

Ni-complex. The R-factor was reduced from 0.33 to 0.15 by two isotropic cycles, and to 0.12 by two further anisotropic cycles, with contributions from hydrogen atoms included in the calculated F-values but not refined. The positions of the hydrogen atoms were estimated from stereochemical considerations, and their isotropic vibrational parameters were taken as equal to those of the atoms to which they were attached. At this stage some serious discrepancies between observed and calculated F-values were noted, particularly for low-order reflexions. Extinction effects could be ruled out as a possible cause for these discrepancies, which were then tentatively ascribed to scattering contributions from occluded molecules of solvent. A difference synthesis showed a diffuse elongated peak lying across the centre of symmetry at $(x, y, z) = (^1/_2, ^1/_2, 0)$ and extending about 2 Å on either side. Integration of this peak gave a count of approximately 28 electrons. If this peak is attributed to solvent (methyl acetate) occupying some of the cavities at $(^1/_2, ^1/_2, 0)$, then the occluded molecules must be statistically distributed over at least four orientations. To avoid introduction of too many extra parameters in the least-squares refinement, the residual density was simulated by several rather simple models, none of which was completely satisfactory. The parameters describing the complex ligand were found to be essentially invariant to incorporation of solvent into the structure model and to changes in the parameters describing the solvent molecules. The analysis was terminated at a final R-factor of 0.10, based on 2620 reflexions with $I \geqslant \sigma(I)$.

Pd-complex. The refined parameters from the analysis of the Ni-complex were used as starting parameters for the refinement of the structure of the Pd-complex. One isotropic cycle, followed by three anisotropic cycles, led to a final R-factor of 0.08, based on 2901 reflexions with $I \geqslant \sigma(I)$. As mentioned earlier, the final difference synthesis showed clear indications of occluded solvent molecules located in the intermolecular cavities at $(x, y, z) = (^1/_2, ^1/_2, 0)$. Because of the difficulties in adequately describing disordered, non-stoichiometric distributions of solvent molecules in terms of a limited number of structural parameters and the essential invariance of the complex ligand (in the case of the Ni-complex) to variation in such parameters, no further calculations were made.

Pt-complex. The refined parameters from the analysis of the Pd-complex were used as starting parameters for the analysis of the Pt-complex. Two anisotropic cycles led to an R-factor of 0.07, based on 5457 reflexions with $I \geqslant 2.5\,\sigma(I)$. Although occluded solvent is probably also present in these crystals, it was again disregarded in the structure model.

Final parameters are listed in Tables 1, 2 and 3 for the Ni-, Pd- and Pt-complexes respectively.

Table 1a

Ni-complex: fractional co-ordinates × 10^4 (standard deviations × 10^4 in parentheses); orthogonal co-ordinates (Å) defined by the best plane through Ni, N(20), N(21), N(22) and N(23); isotropic vibrational parameters (Å^2). For the first six atoms in the Table B = $(B_{11}+B_{22}+B_{33})/3$, where B_{11}, B_{22} and B_{33} are principal axes of the corresponding vibrational tensor

	x	*y*	*z*	*X*	*Y*	*Z*	*B*
Ni	2333 (2)	611 (1)	3586 (1)	−0.003	−0.007	0.002	2.8
Cl	1380 (4)	7300 (4)	7725 (3)	−1.041	5.215	−6.090	5.7
O(1)	1196 (29)	6560 (21)	8238 (20)	−1.238	6.011	−5.038	17.7
O(2)	726 (25)	6924 (22)	6678 (14)	−1.669	3.997	−6.144	17.9
O(3)	2695 (18)	7315 (26)	7617 (21)	0.273	4.752	−6.045	18.2
O(4)	1066 (24)	8509 (14)	8211 (14)	−1.364	5.841	−7.312	13.5
C(1)	3476 (11)	795 (10)	5789 (8)	1.085	2.662	0.797	3.3
C(2)	3196 (11)	140 (10)	6492 (8)	0.788	3.730	1.823	3.5
C(3)	2886 (11)	−1246 (10)	5703 (9)	0.495	2.862	3.072	3.6
C(4)	2414 (11)	−1102 (10)	4678 (8)	0.049	1.587	2.441	3.3
C(5)	1808 (12)	−2164 (11)	3711 (9)	−0.534	0.523	3.218	3.9
C(6)	1676 (11)	−2109 (10)	2757 (8)	−0.642	−0.733	2.747	3.0
C(7)	1169 (12)	−3280 (11)	1726 (9)	−1.125	−1.897	3.632	3.8
C(8)	1543 (12)	−2785 (11)	936 (9)	−0.732	−3.091	2.762	4.2
C(9)	1893 (10)	−1397 (10)	1515 (8)	−0.395	−2.515	1.427	3.0
C(10)	2176 (12)	−598 (11)	1057 (9)	−0.099	−3.266	0.336	3.6
C(11)	2560 (11)	669 (10)	1574 (8)	0.273	−2.771	−0.882	3.2
C(12)	2896 (12)	1544 (11)	1054 (9)	0.622	−3.626	−2.082	3.6
C(13)	3605 (13)	2738 (12)	2017 (10)	1.308	−2.603	−3.005	4.4
C(14)	3119 (11)	2543 (11)	2889 (9)	0.803	−1.298	−2.456	3.3
C(15)	3108 (12)	3489 (11)	3809 (9)	0.770	−0.140	−3.170	3.5
C(16)	2385 (12)	3299 (11)	4517 (9)	0.032	1.002	−2.715	3.2
C(17)	1933 (13)	4336 (12)	5315 (10)	−0.437	2.095	−3.619	4.6
C(18)	1207 (17)	3662 (16)	5820 (13)	−1.174	3.006	−2.690	6.7
C(19)	1089 (13)	2268 (12)	5167 (10)	−1.279	2.275	−1.359	4.3
N(20)	2678 (9)	59 (8)	4715 (7)	0.314	1.474	1.137	3.2
N(21)	2006 (9)	−1064 (9)	2569 (7)	−0.306	−1.154	1.488	3.4
N(22)	2629 (9)	1298 (8)	2622 (7)	0.317	−1.434	−1.169	3.2
N(23)	2031 (9)	2170 (8)	4471 (7)	−0.322	1.121	−1.458	3.2
C(24)	4349 (13)	1800 (12)	6036 (10)	1.951	2.699	−0.191	4.4
C(25)	1944 (13)	517 (13)	6903 (10)	−0.471	4.552	1.455	4.9
C(26)	4399 (15)	349 (14)	7419 (11)	1.966	4.669	2.065	5.6
C(27)	−381 (15)	−3559 (14)	1506 (12)	−2.667	−1.795	3.735	5.9
C(28)	1785 (17)	−4424 (16)	1774 (13)	−0.514	−1.882	5.024	7.1
C(29)	3850 (14)	1024 (13)	328 (11)	1.591	−4.787	−1.704	5.6
C(30)	1602 (14)	1800 (13)	436 (11)	−0.654	−4.167	−2.741	5.2
C(31)	3659 (13)	4733 (12)	4017 (10)	1.317	−0.098	−4.476	4.6
N(32)	4070 (13)	5777 (12)	4189 (10)	1.725	−0.055	−5.577	6.3

The transformation matrix from fractional to orthogonal co-ordinates is defined as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 9.975 & 0.018 & -0.242 \\ -2.406 & -0.851 & 13.440 \\ 0.820 & -11.559 & 4.151 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Old origin in new system: $(X, Y, Z) = (2.244, 4.214, 0.972)$.

Table 1b

Ni-complex: anisotropic vibrational parameters for the nickel atom and the atoms of the perchlorate ion, expressed in the form exp $[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	88	57	32	−5	31	22
Cl	187	118	61	−5	57	57
O(1)	713	334	338	426	645	533
O(2)	501	397	123	357	−135	−31
O(3)	189	580	411	196	237	575
O(4)	586	140	183	158	334	72

Table 2a

Pd-complex: fractional co-ordinates × 10^4 (standard deviations × 10^4 in parantheses); orthogonal co-ordinates (Å) defined by the best plane through Pd, N(20), N(21), N(22) and N(23); isotropic vibrational parameters (Å^2). For the first six atoms in the Table B = $(B_{11}+B_{22}+B_{33})/3$ where B_{11}, B_{22} and B_{33} are principal axes of the corresponding vibrational tensor

	x	y	z	X	Y	Z	B
Pd	2385 (1)	653 (1)	3653 (1)	0.007	0.000	0.003	2.5
Cl	1405 (4)	7202 (3)	7754 (3)	−1.174	6.632	−4.423	4.8
O(1)	1004 (30)	6441 (15)	8178 (17)	−1.559	7.063	−3.230	20.5
O(2)	673 (22)	6858 (17)	6716 (13)	−1.842	5.479	−4.837	15.3
O(3)	2734 (16)	7101 (16)	7546 (17)	0.114	6.049	−4.436	13.4
O(4)	1351 (21)	8439 (11)	8361 (11)	−1.266	7.654	−5.384	11.6
C(1)	3414 (12)	682 (10)	5872 (8)	0.932	2.431	1.691	2.8
C(2)	3007 (12)	− 33 (10)	6485 (9)	0.535	3.102	2.974	2.9
C(3)	2748 (12)	−1381 (10)	5659 (9)	0.333	1.865	3.888	3.0
C(4)	2328 (11)	−1170 (9)	4665 (8)	−0.045	0.817	2.875	2.3
C(5)	1775 (13)	−2187 (11)	3684 (9)	−0.531	−0.461	3.284	3.2
C(6)	1703 (12)	−2138 (10)	2735 (8)	−0.572	−1.573	2.500	2.8
C(7)	1172 (12)	−3272 (11)	1719 (9)	−1.033	−2.925	3.016	3.1
C(8)	1621 (13)	−2759 (11)	944 (10)	−0.587	−3.845	1.843	3.7
C(9)	1959 (12)	−1389 (10)	1550 (8)	−0.304	−2.887	0.735	2.6
C(10)	2203 (12)	− 552 (11)	1085 (9)	−0.070	−3.314	−0.579	3.1
C(11)	2559 (11)	706 (10)	1579 (8)	0.235	−2.520	−1.643	2.5
C(12)	2879 (12)	1554 (10)	1042 (9)	0.545	−3.049	−3.023	3.1
C(13)	3550 (13)	2771 (11)	1968 (9)	1.142	−1.818	−3.701	3.5
C(14)	3099 (12)	2609 (10)	2871 (8)	0.683	−0.665	−2.834	2.8
C(15)	3151 (12)	3524 (10)	3790 (8)	0.690	0.634	−3.182	2.9
C(16)	2554 (12)	3402 (10)	4563 (8)	0.095	1.674	−2.463	2.8
C(17)	2124 (14)	4467 (12)	5365 (10)	−0.362	2.977	−3.085	4.1
C(18)	1584 (19)	3863 (17)	6012 (14)	−0.890	3.745	−1.906	7.1
C(19)	1338 (12)	2482 (11)	5381 (9)	−1.084	2.733	−0.804	3.4
N(20)	2636 (9)	− 11 (8)	4794 (6)	0.227	1.161	1.646	2.5
N(21)	2072 (9)	−1089 (8)	2578 (6)	−0.232	−1.611	1.179	2.5
N(22)	2598 (9)	1387 (8)	2602 (6)	0.231	−1.146	−1.642	2.6
N(23)	2196 (9)	2331 (8)	4630 (7)	−0.234	1.596	−1.186	2.7
C(24)	4386 (14)	1688 (12)	6177 (10)	1.841	2.798	0.786	3.8
C(25)	1664 (14)	291 (12)	6796 (10)	−0.773	3.862	2.810	4.2
C(26)	4191 (14)	145 (12)	7473 (10)	1.642	4.051	3.550	4.1

	x	y	z	X	Y	Z	B
C(27)	– 395 (16)	– 3581 (13)	1467 (11)	– 2.530	– 2.931	3.146	5.0
C(28)	1867 (16)	– 4365 (14)	1781 (11)	– 0.347	– 3.260	4.338	5.0
C(29)	3907 (15)	1097 (13)	377 (11)	1.562	– 4.191	– 2.983	4.8
C(30)	1523 (15)	1674 (13)	367 (11)	– 0.743	– 3.515	– 3.707	4.9
C(31)	3707 (13)	4781 (11)	3943 (9)	1.199	0.970	– 4.501	3.6
N(32)	4156 (12)	5774 (10)	4086 (9)	1.609	1.262	– 5.526	5.0

The transformation matrix from fractional to orthogonal coordinates is defined as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 9.629 & -0.177 & -0.297 \\ -2.337 & 2.257 & 12.011 \\ 0.218 & -11.518 & 7.654 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Old origin in new system: $(X, Y, Z) = (2.169, 3.978, 2.093)$.

Table 2b

Pd-complex: anisotropic vibrational parameters for the palladium atom and the atoms of the perchlorate ion, expressed in the form $\exp[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pd	89	49	31	20	23	32
Cl	179	83	56	14	66	44
O(1)	1139	171	359	376	1047	327
O(2)	501	288	122	223	– 120	8
O(3)	193	263	285	87	172	108
O(4)	628	104	105	114	225	38

Table 3

Pt-complex: fractional co-ordinates $\times 10^4$ (standard deviations $\times 10^4$ in parentheses); orthogonal co-ordinates (Å) defined by the best plane through Pt, N(20), N(21), N(22) and N(23); isotropic vibrational parameters (Å^2)

	x	y	z	X	Y	Z	B
Pt	2395 (1)	649 (1)	3653 (0)	0.009	0.004	0.004	2.4
Cl	1392 (5)	7191 (4)	7748 (4)	– 1.291	6.634	– 4.395	5.0
O(1)	985 (26)	6384 (24)	8205 (20)	– 1.688	7.086	– 3.123	15.3
O(2)	643 (24)	6866 (21)	6731 (18)	– 1.958	5.509	– 4.819	13.2
O(3)	2726 (26)	7074 (23)	7555 (19)	0.005	6.079	– 4.381	13.4
O(4)	1346 (21)	8465 (19)	8374 (16)	– 1.393	7.687	– 5.381	10.0
C(1)	3413 (14)	683 (12)	5859 (10)	0.885	2.426	1.683	3.0
C(2)	3028 (14)	– 27 (12)	6499 (11)	0.500	3.113	2.984	3.3
C(3)	2761 (15)	– 1367 (13)	5672 (11)	0.310	1.875	3.884	3.7
C(4)	2323 (13)	– 1183 (12)	4675 (10)	– 0.069	0.822	2.897	3.1
C(5)	1741 (15)	– 2187 (13)	3695 (11)	– 0.562	– 0.453	3.286	3.4
C(6)	1700 (14)	– 2141 (12)	2730 (10)	– 0.556	– 1.589	2.490	3.0
C(7)	1189 (15)	– 3260 (13)	1720 (11)	– 0.977	– 2.942	2.990	3.6
C(8)	1626 (16)	– 2779 (14)	932 (12)	– 0.529	– 3.872	1.839	3.9
C(9)	1976 (14)	– 1386 (12)	1559 (10)	– 0.251	– 2.878	0.725	3.2
C(10)	2220 (15)	– 569 (13)	1071 (11)	– 0.011	– 3.328	– 0.585	3.5
C(11)	2547 (14)	697 (12)	1580 (10)	0.252	– 2.500	– 1.643	3.1
C(12)	2881 (15)	1548 (13)	1035 (11)	0.581	– 3.031	– 3.035	3.5

	x	y	z	X	Y	Z	B
C(13)	3539 (16)	2767 (14)	1955 (12)	1.145	−1.796	−3.716	4.1
C(14)	3090 (14)	2598 (12)	2858 (10)	0.674	−0.653	−2.837	3.0
C(15)	3166 (14)	3528 (12)	3786 (10)	0.683	0.654	−3.191	3.1
C(16)	2572 (14)	3396 (12)	4588 (10)	0.077	1.715	−2.435	3.1
C(17)	2161 (17)	4464 (15)	5377 (13)	−0.380	2.997	−3.065	4.3
C(18)	1656 (24)	3875 (22)	6071 (18)	−0.887	3.805	−1.864	6.5
C(19)	1359 (16)	2467 (14)	5389 (11)	−1.111	2.731	−0.774	3.8
N(20)	2646 (11)	− 10 (9)	4792 (8)	0.212	1.159	1.643	2.7
N(21)	2066 (11)	−1081 (9)	2571 (8)	−0.220	−1.617	1.155	2.9
N(22)	2576 (11)	1353 (10)	2592 (8)	0.219	−1.144	−1.619	3.0
N(23)	2244 (12)	2332 (10)	4633 (8)	−0.219	1.598	−1.182	3.1
C(24)	4392 (16)	1677 (14)	6173 (12)	1.792	2.812	0.800	4.0
C(25)	1641 (18)	303 (15)	6802 (13)	−0.858	3.861	2.809	4.6
C(26)	4172 (18)	145 (16)	7463 (13)	1.552	4.053	3.551	4.8
C(27)	− 422 (20)	−3583 (17)	1466 (14)	−2.510	−2.962	3.133	5.2
C(28)	1867 (20)	−4406 (17)	1764 (15)	−0.301	−3.304	4.356	5.3
C(29)	3896 (19)	1079 (17)	361 (14)	1.601	−4.171	−2.993	5.2
C(30)	1489 (20)	1638 (17)	344 (15)	−0.729	−3.528	−3.699	5.3
C(31)	3699 (16)	4763 (14)	3935 (12)	1.163	0.998	−4.488	3.9
N(32)	4146 (16)	5767 (14)	4096 (12)	1.564	1.322	−5.509	5.4

The matrix for transformation from fractional to orthogonal coordinates is defined as follows:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 9.633 & -0.216 & -0.472 \\ -2.224 & 2.302 & 11.970 \\ 0.206 & -11.508 & 7.695 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Old origin in new system: $(X, Y, Z) = (2.112, 3.986, 2.110)$.

Discussion. – From Figs. 1–3 it is clear that the topographies of the Ni-, Pd- and Pt-seco-corrinoid complexes are very similar; in fact, the Pt- and Pd-complexes are virtually superposable, the differences between corresponding crystal and molecular

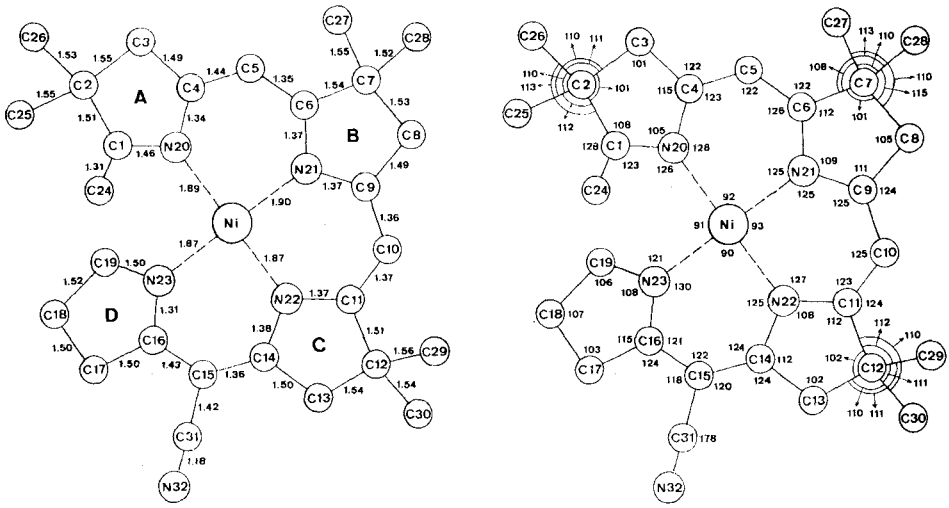


Fig. 1. *Ni-complex: bond lengths and angles*

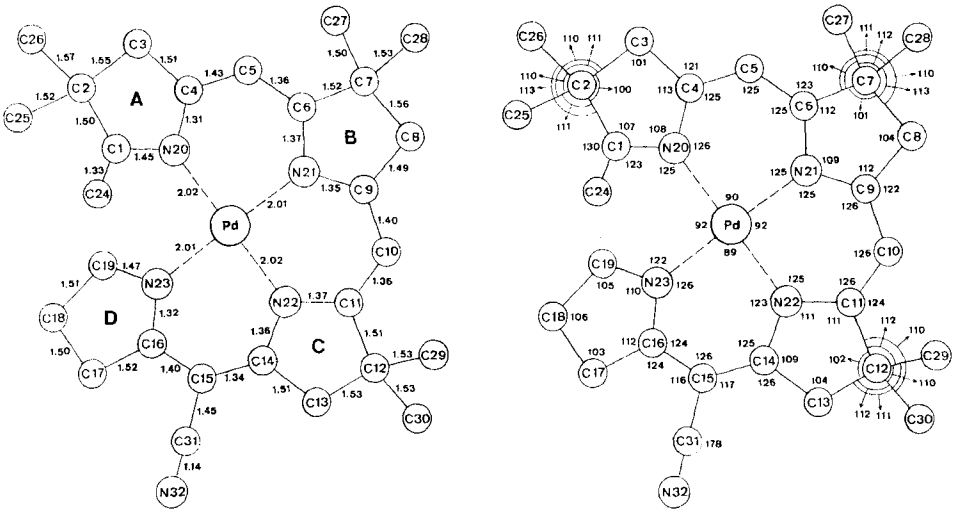


Fig. 2. *Pd-complex: bond lengths and angles*

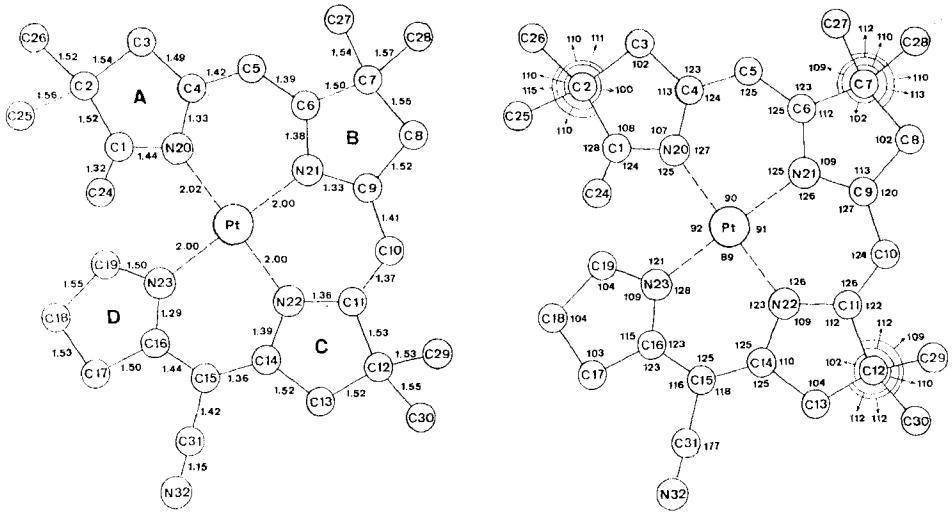


Fig. 3. *Pt-complex: bond lengths and angles*

parameters being hardly greater than the experimental error. The Ni-complex, although similar in overall structure, shows significant structural differences from the other two, differences that may be relevant to the different chemical behaviour.

The structural similarities and differences in the three complexes may be directly related to the coordination requirements of the metal atoms. The Ni-N distances lie between 1.87 Å and 1.90 Å, roughly the same range as observed in other Ni-corrinoid [3] and seco-corrinoid complexes [4]. As in the other Ni-complexes, diagonally opposite pairs of N-atoms are alternately above and below the mean coordination plane. The displacements are 0.31–0.32 Å (somewhat greater than in the other Ni-complexes),

producing a marked distortion of the usual planar coordination in the direction of a flattened tetrahedral coordination. The metal-nitrogen distances are 2.01–2.02 Å in the Pd-complex, and 2.00–2.02 Å in the Pt-complex—virtually identical; the tendency towards tetrahedral coordination persists in these two complexes but is less marked. The displacements of the N atoms from the mean coordination plane are 0.23 Å for the Pd-complex and 0.21–0.22 Å for the Pt-complex—again virtually identical.

Although most 4-coordinated complexes of Ni^{II} are planar and diamagnetic, it is known that paramagnetic, tetrahedrally coordinated complexes are obtained if bulky substituents on the ligands would cause steric overcrowding in the planar form. For example, although bis-(N-methyl-salicylaldiminato)-Ni^{II} is planar and diamagnetic [5], the N-isopropyl and N-*sec*-butyl derivatives show conformational equilibria where the amount of tetrahedral, paramagnetic species increases with increasing temperature [6]. Observed Ni-N distances are 1.90–1.92 Å in planar complexes with bidentate chelates and 1.95–1.99 Å in corresponding tetrahedral complexes [7]. Whereas bis-(N-isopropyl-3-ethyl-salicylaldiminato)-nickel(II) has been shown to be tetrahedral in the solid state [7], the corresponding palladium(II) complex is planar with Pd-N distances of 2.03 Å [8]. A comparison of non-bonded N... N distances in various corrinoid and seco-corrinoid metal complexes (summarized in Fig. 4) reveals that, apart from the N... N distance across the A/D ring junction (2.45–2.46 Å), the distances in the Ni-complexes are distributed around a mean value of about 2.7 Å, whereas in the more nearly planar Pd- and Pt-complexes the N... N distances are appreciably longer, about 2.85 Å. Although no firm conclusion can be reached from this evidence, it would appear that the greater resistance of Pd^{II} (and Pt^{II}) to tetrahedral distortion does not necessarily result from an increased energy difference (compared with Ni^{II}) between the planar and tetrahedral states, but may merely be a consequence of the reduction in steric strain associated with expansion of the metal-ligand distances. The observed similarities and differences in the isomorphous series

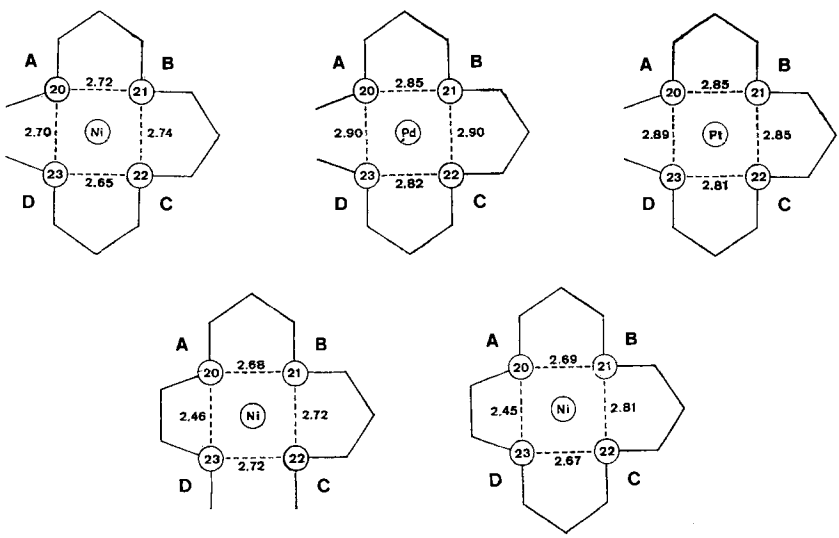


Fig. 4. *Summary of non-bonded N... N distances in various corrinoid and seco-corrinoid complexes*

of seco-corrinoid complexes with Ni^{II}, Pd^{II} and Pt^{II} would be consistent with this picture.

Although minor differences occur between the lengths of corresponding bonds within the complex ligand in the three structures (Figs. 1, 2, 3), they are not statistically significant. The largest differences are about 0.05 Å and occur, with one exception (C(9)–C(10)), for bonds to the peripheral methyl groups. These are just the bonds where one would expect little or no change in bond length from one complex to another; they are also among the bonds with the largest estimated standard deviations attached to the observed lengths (excluding the Cl-O bonds in the perchlorate anions). For the conjugated 15-centre, 16-electron system, extending from C(24) to N(23), the observed bond lengths, together with the lengths averaged over the three complexes, are given in Table 4. The three individual sets of observations show no significant differences from one another. The mean bond lengths, and, for comparison, HMO bond orders calculated with standard values of the empirical parameters [9] are also given in Table 4 [10]. The agreement is as good as can be expected.

Table 4. *Observed bond lengths* (in Å) *and calculated HMO π-bond orders* ($\alpha_N = \alpha_C + 1.5\beta, \beta_{CN} = \beta$) *for system* C^1-C^2-N^3-C^4-C^5-C^6-N^7-C^8-C^9-C^{10}-N^{11}-C^{12}-C^{13}-C^{14}-N

	Ni-complex	Pd-complex	Pt-complex	Mean observed	Bond Order
Bond 1	1.314	1.333	1.323	1.323	0.911
2	1.457	1.453	1.435	1.448	0.390
3	1.336	1.305	1.328	1.323	0.571
4	1.441	1.427	1.421	1.430	0.630
5	1.346	1.361	1.387	1.365	0.696
6	1.369	1.365	1.377	1.370	0.500
7	1.365	1.353	1.333	1.350	0.525
8	1.357	1.402	1.406	1.388	0.663
9	1.367	1.362	1.369	1.366	0.666
10	1.369	1.374	1.357	1.367	0.521
11	1.382	1.363	1.390	1.378	0.503
12	1.361	1.344	1.355	1.353	0.698
13	1.433	1.398	1.437	1.423	0.628
14	1.312	1.321	1.293	1.309	0.592

In general the conformation of a five-membered ring is very sensitive to the forces acting on it, and hence to its environment. The observed conformations of rings A, B and C hardly change from one complex to another, as is evident from the torsion angle patterns shown in Table 5. There is a formal change in the conformation of ring D, from a very flattened envelope form in the Ni-complex to a rather flattened C_2 form in the Pd- and Pt-complexes, but the ring is so nearly planar that the difference is more apparent than real.

In none of the three complexes does the metal atom lie exactly in any of the four planes defined by the ring N-atoms and their bonded C-neighbours. As mentioned earlier, the four N-atoms lie on the vertices of a rather flattened tetrahedron whose centre is occupied by the metal atom. If now the mid-points of the lines joining the 2, 5-positions of the rings are taken as reference points, these also lie on the vertices of a tetrahedron that is distinctly *less* flattened than the N-atom tetrahedron. As for so

Table 5. *Torsion angles and bond-angle sums in 5-membered rings* (degrees)

	Ring A Ni	Pd	Pt		Ring B Ni	Pd	Pt
N(20)-C(1)	−23	−25	−23	N(21)-C(6)	−5	−5	−6
C(1)-C(2)	+30	+32	+31	C(6)-C(7)	+11	+13	+13
C(2)-C(3)	−25	−28	−27	C(7)-C(8)	−13	−15	−14
C(3)-C(4)	+14	+15	+16	C(8)-C(9)	+11	+14	+12
C(4)-N(20)	+5	+5	+4	C(9)-N(21)	−4	−6	−5
Sum of bond angles	531	529	530	Sum of bond angles	538	538	538
Envelope with $C(2)$ as 'flap'				Rather flat C_2 form			

	Ring C Ni	Pd	Pt		Ring D Ni	Pd	Pt
N(22)-C(11)	−6	−8	−8	N(23)-C(16)	+8	+7	+8
C(11)-C(12)	+17	+17	+17	C(16)-C(17)	+1	+6	+8
C(12)-C(13)	−20	−18	−17	C(17)-C(18)	−9	−16	−19
C(13)-C(14)	+19	+15	+14	C(18)-C(19)	+13	+20	+23
C(14)-N(22)	−9	−5	−4	C(19)-N(23)	−13	−17	−20
Sum of bond angles	536	536	537	Sum of bond angles	538	536	535
Rather flat C_2 form				Ni: Very flat envelope with C(19) as 'flap' Pd, Pt: Rather flat C_2 form			

many other features, the exact relationships holding in the Ni-complex are slightly different from those in the Pd- and Pt-complexes, which are virtually identical. The deviations from trigonal planar bonding at the N atoms are undoubtedly connected with repulsions between non-bonded atoms in the equilibrium structures of the molecules, but the interactions are so complex that a detailed strain-analysis could be made only on the basis of a large set of empirical potential functions, which are at present not available.

The main source of strain is obviously the repulsions between the non-bonded atom pairs, C(1)... C(19), C(24)... C(19), C(1)... H(19α) and C(24)... H(19α), involved in the photochemical cyclization step. Fig. 5 illustrates the spatial relationships of the atoms in the region of interest. The C(1)... C(19) distance is virtually constant at 3.2 Å; the C(24)... C(19) distance is 3.46 Å in the Ni-complex and somewhat shorter (3.33, 3.30 Å) in the Pd- and Pt-complexes. It is unfortunate that the position of the critical hydrogen atom H(19α) could not be determined directly, but has had to be estimated from stereochemical considerations; assumptions: C–H = 1.10 Å, H–C(19)-H = 109,5° bisected by plane C(18)C(19)N(23) and normal to this plane. This model leads to C(24)... H(19α) distances of 2.97 Å for the Ni-complex and of 2.70 Å for the Pd- and Pt-complexes, and to C(1)... H(19α) distances that are even shorter—2.48, 2.39 and 2.36 Å in the Ni-, Pd- and Pt-complexes respectively. The latter distances, particularly those in the Pd- and Pt-complexes are markedly shorter than the *Van der Waals* minima in any of the empirical C... H potential curves that have been proposed by various authors (see [11] for a review) and would correspond to appreciable repulsion energies of 0.5–1.0 kcal. mole^{-1}.

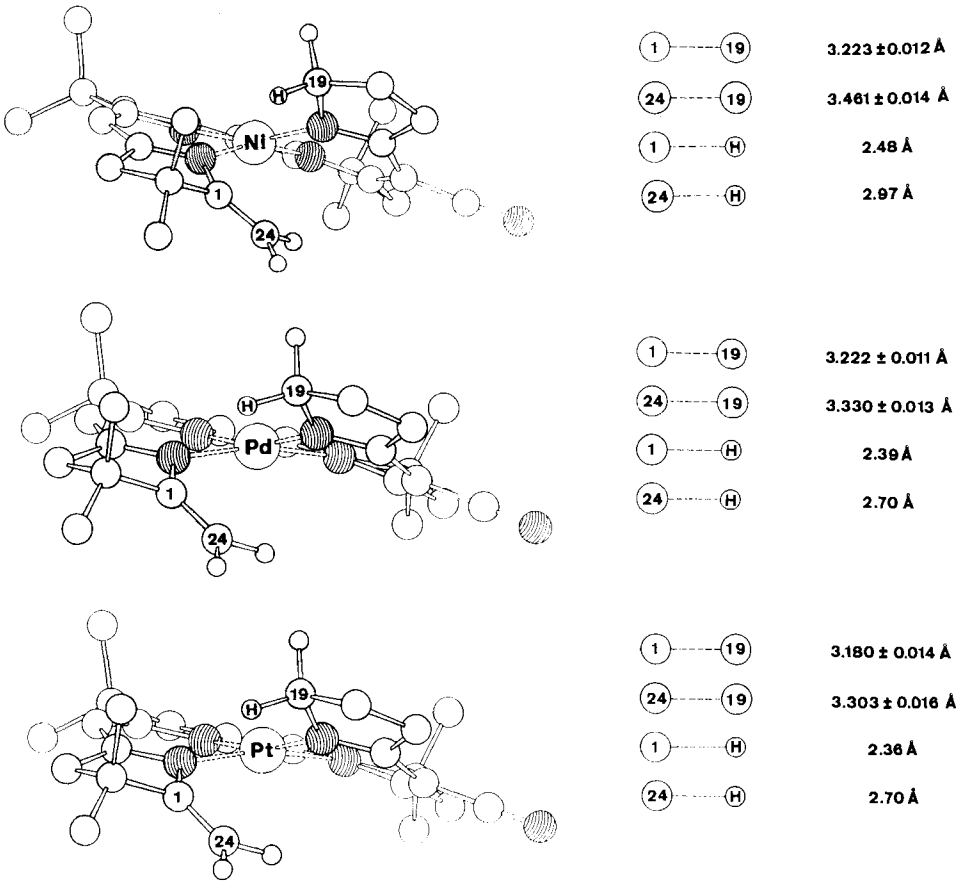


Fig. 5. *View of the three complexes, looking down the* Y-*axes of the orthogonal coordinate systems defined in Tables 1, 2, 3.*

In each case the X-axis points downward, the Z-axis to the left. A 15°-rotation of the Ni-complex in the YZ-plane would make the view even more similar to those of the Pd- and Pt-complexes. Some interatomic distances of interest are given.

Another aspect of the spatial relationships between the atoms involved in the cyclization step is shown in Fig. 6. It is seen that in the Pd- and Pt-complexes the migrating H atom is almost vertically above C(1) with respect to the mean plane of the double-bond system, *i.e.* it lies almost on the line of maximum electron density of the p-orbital formally attached to C(1). In the Ni-complex this H atom is somewhat displaced *away from* C(24), the displacement being nearly antiparallel to the C(1)–C(24) bond direction.

Any appreciable repulsion between C(1) and H(19α) should have the effect of pushing C(1) out of the plane through N(20), C(2) and C(24), away from H(19α); a detailed examination shows, however, that C(1) is actually displaced out of this plane *towards* H(19α) in all three cases. From orbital symmetry considerations it can be

shown that in the ground state of the molecule the *s*-orbital of the hydrogen atom in question has a bonding frontier–orbital interaction with both C(1) and C(19). The observed deviations from the plane are small–0.03, 0.04 and 0.05 Å for the Ni-, Pd-

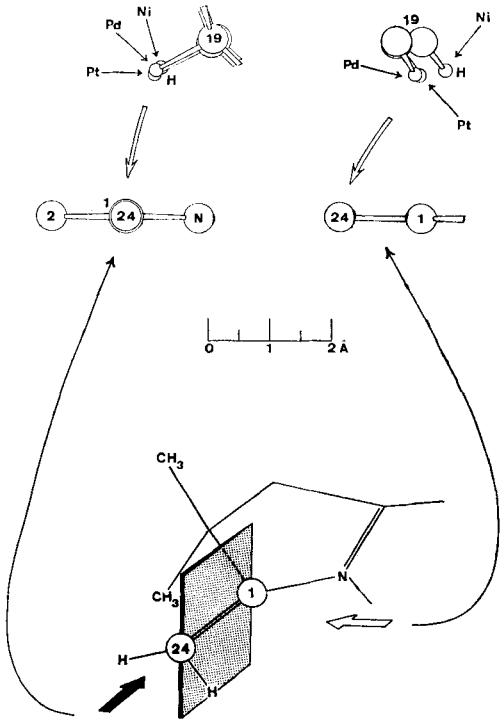


Fig. 6. *Spatial relationship of the migrating H atom on C(19) and the exocyclic methylidene group C(24)* Views are shown looking along and perpendicular to the double bond C(1)–C(24).

and Pt-complexes respectively—but significant and all in the same direction; we are tempted to describe the C(19)–H... C(1) interaction as weakly bonding.

Any attempt to correlate the observed structural similarities and differences between the Ni-, Pd- and Pt-complexes with their differences in chemical behaviour would be premature at present and must await the results of further chemical, crystallographic and spectroscopic studies now in progress in several laboratories.

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10. Studies on Solubilization (Part I) Note on the Synthesis of Some Quaternary N-(ω-Aryloxyalkyl) Piperidinium, Pyridinium, Benzyl-dimethyl-ammonium, and Trimethyl-ammonium Bromides

by **R. K. Joshi**[1]), **L. Krasnec**, and **I. Lacko**
Scientific Research Institute, Faculty of Pharmacy, Komensky University, Bratislava (Czechoslovakia)

(15. VIII. 70)

Summary. A series of new N-(ω-aryloxyalkyl) piperidinium, pyridinium, benzyl dimethyl ammonium, and trimethyl ammonium bromides is described.

For the study of the mechanisms of solubilization of organic substances in water, we have synthesized a series of compounds with the general formula Ar–O–$(CH_2)_n$–$\overset{\oplus}{N}$ $Br^{\ominus}$ (see tables II and III).

Table I. *Physical Properties of new α-bromo-ω-aryloxy-alkanes*
Ar—O—$(CH_2)_n$—Br

Ar	n	Yield, % (not optimized)	B.p. °C/Torr	M.p. °C	Calcd., %			Found, %		
					C	H	Br	C	H	Br
4-$(CH_3)_3C \cdot C_6H_4$	4	75.8	138–140 (0.05)		58.95	7.42	28.02	58.72	7.55	27.90
4-$[(CH_3)_3C \cdot CH_2 \cdot (CH_3)_2C] \cdot C_6H_4$	4	53.7	168–170 (0.35)		63.34	8.56	23.41	63.39	8.82	23.28
4-$C_9H_{19} \cdot C_6H_4$	4	27.5	170–175 (0.5)		64.22	8.79	22.49	63.57	8.90	22.14
3-$(CH_3O) \cdot C_6H_4$	4	66.9	148–149 (0.05)		50.98	5.83	30.84	51.20	6.10	31.40
4-$C_6H_5 \cdot C_6H_4$	4	77.5	184–185 (0.5)	78–79 (petr. ether)	62.96	5.61	26.18	63.12	5.63	26.20
1-$C_{10}H_7$	4	53.7	170–175 (0.05)	38 (ethanol)	60.23	5.42	28.62	59.79	5.58	28.25

These quaternary ammonium salts were prepared by treating eleven 1-alkylpiperidines, 1-cyclohexylpiperidine, pyridine, benzyldimethylamine, and trimethylamine with seventeen α-bromo-ω-aryloxy-alkanes. The α-bromo-ω-aryloxy-alkanes were prepared by condensing [1] a phenol with an α,ω-dibromoalkane. Purity of the compounds from table III was further confirmed by paper chromatography [2].

[1]) Present adress: Pharmazeutisches Institut der ETHZ, Clausius-Strasse 25, 8006 Zurich (Switzerland).