Kinetic studies on the single Cl^- equilibration with $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ indicate a process too fast to monitor by the stopped-flow method, $k > 2 \times 10^4$ M^{-1} s^{-1} at 25 °C, I = 2.00 M ($HClO_4$). This compares with a rate constant for octahedral 1:1 Cl^- substitution of H_2O on $[Fe(H_2O)_6]^{3+}$ of 9.4 M^{-1} s^{-1}.[22] Substitution on $[Fe(H_2O)_6]^{2+}$ is faster, with the rate constant for H_2O solvent exchange of 4×10^6 s^{-1}.[23,24]

The cuboidal aqua ions $[Mo_4S_4(H_2O)_{12}]^{n+}$ (n = 4–6) have lower (average) oxidation states, 3.0, 3.25, and 3.5, as compared to the Mo^{IV}_3 state of the $[Mo_3S_4(H_2O)_9]^{4+}$ ion. The same sort of trend in stable oxidation states is observed for Fe_4S_4 and Fe_3S_4 clusters. In the present case, conversion of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Fe(H_2O)_6]^{2+}$ requires the release of two electrons, as confirmed by the stoichiometry of the reactions with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ as oxidants. A single rate determining step is observed, first-order in each reactant, and isosbestic points are retained. This indicates two-stage reactions, the second step faster in each case, as indicated in (10) and (11) and (13) and (14). The 5+ ion has not previously been identified and is to be regarded as a reactive intermediate.

It would be unusual if the $[Co(dipic)_2]^-$ oxidant, with only carbonyl O atoms as potential bridging ligands, reacted by other than an outer-sphere electron-transfer process. It is significant also that there is no $[H^+]$ dependence for reaction with this oxidant. The observation of an $[H^+]$ dependence of the kind $a + b[H^+]^{-1}$, in the case of the $[Fe(H_2O)_6]^{3+}$ reaction, with a (4.8 M^{-1} s^{-1}) and b (4.0 s^{-1}) of similar magnitude, supports an inner-sphere involvement of $[Fe(H_2O)_5OH]^{2+}$. Taking into account the acid dissociation constant for $[Fe(H_2O)_6]^{3+}$, $K_a = 1.0 \times 10^{-3}$ M at 25 °C, I = 2.0 M ($NaClO_4$), the second-order rate constant from b is 4.0×10^3 M^{-1} s^{-1}. This is probably too fast to be occurring at other than the labile Fe site on $[Mo_3FeS_4(H_2O)_{10}]^{4+}$.

A comparison of outer-sphere rate constants for $[Co(dipic)_2]^-$ (k_{Co}) and $[Fe(H_2O)_6]^{3+}$ (k_{Fe}) oxidations of $[Mo_4S_4(edta)_2]^{2-}$ (17.8 and 6.4×10^4 M^{-1} s^{-1}, respectively, the latter at 10 °C)[25] and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (87 and 4.8 M^{-1} s^{-1}, respectively) indicates k_{Co} values of similar magnitude, whereas k_{Fe} is very much influenced by work terms.[26] Thus the favorable charge interaction (3−, 3+) for the reaction with $[Mo_4S_4(edta)_2]^{2-}$ gives a rate constant of 6.7×10^4 M^{-1} s^{-1}, whereas the unfavorable charge combination (4+, 3+) for $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ gives a rate constant of 4.8 M^{-1} s^{-1}. From calculations we were able to carry out, the $[Mo_3FeS_4(H_2O)_{10}]^{5+/4+}$ reduction potential is probably very similar to that of the $[Mo_4S_4(edta)_2]^{2-/3-}$ couple at 0.65 V.

Harris in a recent review[1] has considered the structure, bonding, and electron counts in cubane-type clusters having M_4S_4, $M_2M'_2S_4$ and $M_3M'S_4$, cores. With H_2O ligands, which are not π donors, the T_d splitting is larger, causing the nonbonding e orbitals of the Fe to be lower than the bonding orbitals. The 14 metal-based electrons of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ will occupy metal–metal bonding and nonbonding orbitals, the HOMO being a bonding orbital. Oxidation will, therefore, result in a destabilization of the cube. The fact that the 5+ Mo_3FeS_4 cube is highly reactive with a second mole of oxidant and then breaks down to give $Mo_3S_4^{4+}$ is consistent with the removal of M–M bonding. An alternative interpretation would be that rapid decomposition occurs to yield $Mo_3S_4^{3+}$ (a strong reductant) and Fe^{2+}, and this is followed by rapid reaction of $Mo_3S_4^{3+}$ with Fe^{3+}.

Acknowledgment. We are grateful to the U.K. Science and Engineering Research Council for a studentship (to P.W.D.) and Professor C. E. Johnson of the University of Liverpool for discussions.

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Multinuclear (^{195}Pt, ^{15}N, ^{13}C) NMR Studies of the Reactions between *cis*-Diaminediaquaplatinum(II) Complexes and Aminomalonate

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The reactions between *cis*-$PtAm_2(H_2O)_2^{2+}$ (Am = RNH_2, aziridine; Am_2 = ethylenediamine, 1,2-diaminocyclohexane) and aminomalonate (amal) show that initially the O,O chelate with the 1,1-dicarboxylic group is formed and that subsequently the kinetic product isomerizes to yield the thermodynamically stable N,O chelate. The identity of the thermodynamic product was established by ^{195}Pt, ^{15}N, and ^{13}C NMR spectroscopy. The formation of the unidentate intermediate adduct $[PtAm_2(H_2O)(amal\text{-}O)]^+$ could not be observed by ^{15}N NMR spectroscopy due to the fast transformation to give the $[PtAm_2(amal\text{-}O,O)]^+$ chelate. ^{195}Pt NMR studies also show that 22-h reactions in DMF between *cis*-$PtAm_2LL$ (L = DMF, NO_3^-) and amidomalonates resulted in isomeric mixtures in which the O,O:N,O ratio ranged between 3:2 and 5:1.

Introduction

cis-Diamminedichloroplatinum(II) (Cisplatin—see Figure 1) is a very effective drug against ovarian, testicular, bladder, and head and neck cancers.[1-3] Its major drawbacks include severe toxicity, acquired resistance, and ineffectiveness against major forms of the disease such as colon and breast cancers.[4,5] Many attempts have been made to prepare platinum complexes with improved therapeutic properties, but only few have been successful.[6,7] These second-generation antitumor platinum drugs were patterned after the classic structure–activity relationships[8] and closely resemble Cisplatin except that the chloride ligands have been replaced by 1,1- or 1,2-dicarboxylates (see examples

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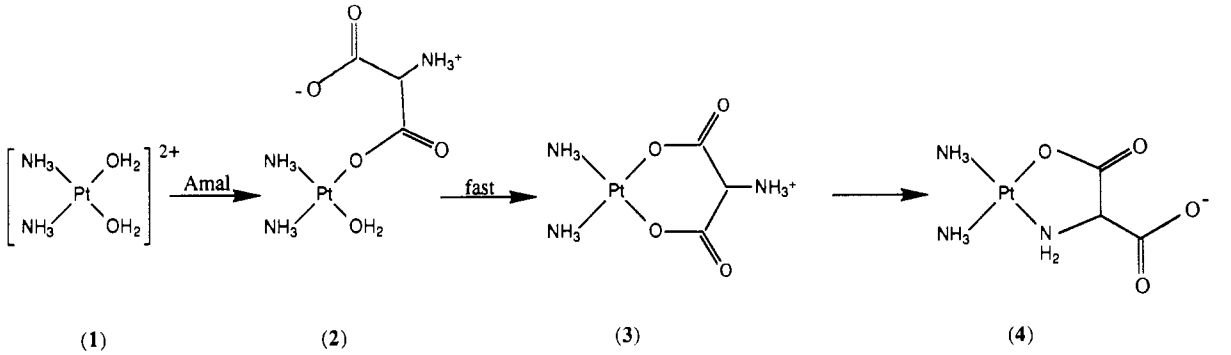
Scheme I



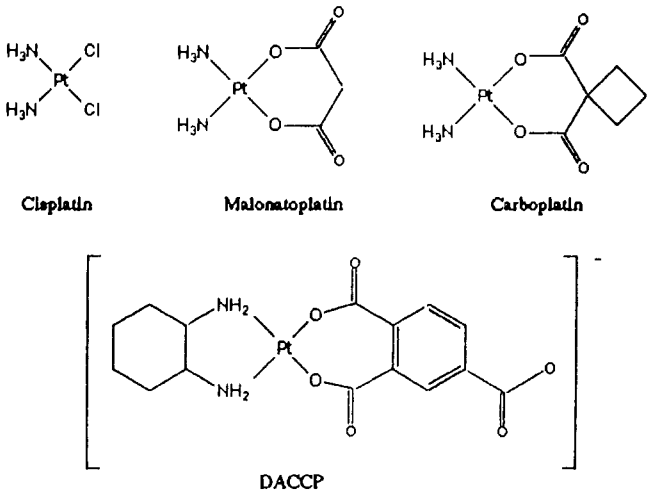


Figure 1. Cisplatin and several second-generation antitumor drugs.

in Figure 1).[9-12] Reduced nephrotoxicity is the major advantage of the second-generation platinum drugs such as Carboplatin.[13,14] Nevertheless, even the improved drugs still suffer from a narrow range of activity and from the phenomenon of acquired resistance. Thus, the search for the third-generation anticancer platinum drugs still continues.

Many of the attempts aimed at developing third-generation platinum anticancer drugs have focused on the enhancement of the aqueous solubility of diamine dicarboxylate complexes.[15,16] Some of these attempts included the binding of the diaminediaquaplatinum moiety to iminodiacetate and its derivatives.[17] Subsequent work has shown that iminodiacetates bind the platinum through the imino nitrogen and one carboxylate oxygen rather than through both carboxylate groups.[18,19] In previous studies we have reacted aminomalonate (amal) with diaminediaquaplatinum(II) complexes $\{[PtAm_2(H_2O)_2]^{2+}\}$ and obtained water-soluble products that displayed considerable in vivo activity.[20,21]

Table I. ^{195}Pt Chemical Shifts for $PtAm_2(amal)$ Complexes

compd no.	compd	$-\delta$, ppm
4	$(H_3N)_2Pt(amal)$	2160
5	(en)Pt(amal)	2426
6	(DACH)Pt(amal)[a]	2370
		2394
7	(aziridine)$_2$Pt(amal)	2324
8	(c-propylamine)$_2$Pt(amal)	2228
9	(c-butylamine)$_2$Pt(amal)	2270
10	(c-pentylamine)$_2$Pt(amal)	2237
11	(c-hexylamine)$_2$Pt(amal)[b]	
12	(isopropylamine)$_2$Pt(amal)	2248
13	(*n*-propylamine)$_2$Pt(amal)	2243

[a] The two signals result from a mixture of the DACH isomers. [b] The complex was insoluble in common solvents.

One of the approaches to broadening the spectrum of activity included attempts to alter the biodistribution of the drug by directing it to specific organs.[22,23] Recently, the $PtAm_2^{2+}$ moiety was tethered to various functionalized steroidal hormones, through 1,1-dicarboxylate linkages, some of which had amide nitrogens adjacent to the dicarboxylate unit.[24] In view of the ability of divalent platinum to bind the nitrogen atom of *N*-acetylglycine,[25] the exact identity of the platinum–steroid complexes remains an interesting question.

For many years stable triamine monochloro complexes such as $[Pt(NH_3)_3Cl]^+$ and $[Pt(dien)Cl]^+$ were considered inactive. However, the recent report by Hollis et al. has demonstrated the antitumor activity of cationic triamine monochloro complexes in in vivo model systems[26] and raises the question of the identity of the active species in the diamine(aminomalonato)platinum(II) system. While the activity displayed by the aminomalonato complexes was attributed by some researchers to impurities containing platinum chloride complexes,[27] the exact nature of the aminomalonato complexes has yet to be elucidated by unequivocal techniques such as ^{195}Pt and ^{15}N NMR spectroscopy or X-ray crystallography. Also, the solution chemistry, including possible isomerization reactions, has not yet been explored. In this paper we report solution studies of the reaction of aminomalonate with several diaminediaquaplatinum(II) complexes and the complete characterization of the products by multinuclear NMR spec-

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troscopy. Likewise, we report the ^{195}Pt NMR characterization of some of the platinum–steroid complexes that we have previously reported.[24]

Experimental Section

Starting Materials. K_2PtCl_4 and $^{15}NH_4Cl$ were purchased from Aldrich Chemical Co. Inc. and were used without further purification.

NMR Measurements. ^{195}Pt NMR spectra (42.935 MHz) were measured on a Bruker WP-200 spectrometer using a 10-mm broad-band probehead. Typical acquisition parameters included an 8-μs pulse with a spectral width of 125 000 Hz. Most spectra were processed by using a 200-Hz line broadening. The ^{195}Pt chemical shifts were referenced externally to K_2PtCl_4 in D_2O at −1624 ppm. Other ^{195}Pt spectra were measured at 64.374 MHz on a Varian VXR-300s spectrometer equipped with a 5-mm computer switchable probehead. Typical acquisition parameters include a 100 000 Hz sweep width, a 7-μs pulse width, and a 200-Hz line broadening. ^{15}N NMR spectra were measured at 30.406 MHz on the Varian VXR-300s spectrometer. All ^{15}N spectra were acquired with broad-band decoupling of the protons (WALTZ-16) and were referenced externally to $^{15}NH_4Cl$ at 0 ppm. A line broadening of 0.3 Hz was applied for processing. The ^{13}C NMR (75.429 MHz) were measured in D_2O with dioxane serving as an internal reference at 67.8 ppm. The spectra were acquired with broad-band decoupling and long recycle delays ($d1$ = 6 s) to facilitate the observation of the carbonyl carbons. The data were processed with a 1-Hz line broadening.

Preparation of Complexes. The preparation of the aminomalonato complexes (**4–13**) has been detailed in ref 20, and that of the steroidal complexes (**14–19**), in ref 24.

Results and Discussion

$PtAm_2$(amal) Complexes. The (aminomalonato)diamineplatinum(II) complexes were characterized by elemental analyses and by multinuclear NMR (^{195}Pt, ^{15}N, ^{13}C). For example, in the synthesis of **4** (Table I), the diamminediaquaplatinum(II) starting material **1** (Scheme I) was prepared in situ by overnight reaction of 1 equiv of Ag_2SO_4 with 1 equiv of $Pt(NH_3)_2I_2$, as has been previously reported.[20] The ^{195}Pt NMR spectrum of the product showed two resonances located at −1551 and −1587 ppm, which can be attributed to $Pt(NH_3)_2(SO_4)(H_2O)$ and $[Pt(NH_3)_2(H_2O)_2]^{2+}$, respectively.[28] Upon reaction with 1 equiv of the Ba salt of aminomalonate a fine white precipitate of $BaSO_4$ formed and was filtered off. Subsequently the resonance observed at −1551 ppm vanished and only a single resonance at −1587 ppm, corresponding to $[Pt(NH_3)_2(H_2O)_2]^{2+}$, remained. As the reaction progressed, a peak at approximately −1700 ppm started growing in, indicating the formation of the 1,1-dicarboxylate complex (**3**). As the experiment progressed further, the signal in the −1700 ppm region disappeared and, finally, only a single resonance was observed at around −2100 ppm. This resonance is assigned to the thermodynamic product of the reaction, which is an N,O chelate (**4**; see Scheme I).

The ^{195}Pt NMR spectra of all the diamine(aminomalonato)platinum(II) complexes previously reported by us[20] have been measured, and the results are listed in Table I. It is clear that in all cases the Pt coordination sphere, of the thermodynamic, product, comprises three nitrogen atoms and one oxygen atom indicating that an N,O chelate was obtained. The chemical shifts measured for the aminomalonate complexes are in agreement with those observed for N,O chelation of diamineplatinum complexes by α-amino acids.[29,30] This result is not surprising, since the ^{195}Pt chemical shifts are sensitive to the nature of the donor ligands and the chelating moiety of the aminomalonate is nearly identical with those of α-amino acids.[31]

We had chosen to measure the ^{15}N NMR spectra of the complexes, since they can provide us with information that is not easily accessible by ^{195}Pt NMR spectroscopy. We prepared the ^{15}N-labeled $Pt(^{15}NH_3)_2I_2$ according to published procedures.[32] The products obtained from the reaction of $Pt(^{15}NH_3)_2I_2$ and Ag_2SO_4

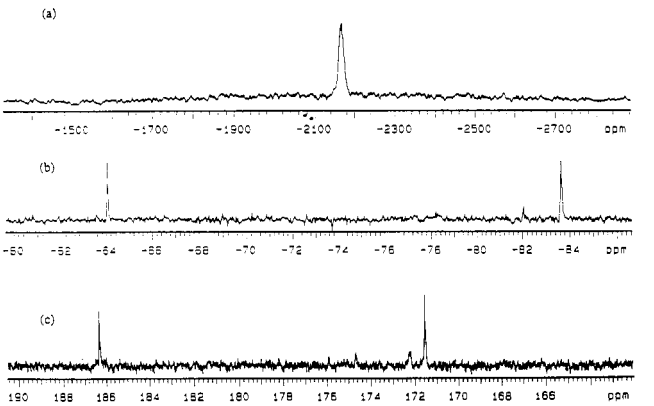

Figure 2. Multinuclear NMR spectra of $Pt(NH_3)_2$(amal-*N,O*): (a) ^{195}Pt NMR spectrum; (b) ^{15}N NMR spectrum; (c), ^{13}C NMR spectrum (carbonyl region).

show three resonances at −84.55, −85.19, and −85.36 ppm; the first corresponds to the amine trans to SO_4, the second to the amine trans to H_2O, and the third to $[Pt(^{15}NH_3)_2(H_2O)_2]^{2+}$. The ^{195}Pt–^{15}N coupling constant of $[Pt(^{15}NH_3)_2(H_2O)_2]^{2+}$ was found to be 384 Hz. By ^{15}N NMR spectroscopy we tried to observe the ligation of the aminomalonate and to see the formation of the unidentate adduct (**2**) prior to formation of the O,O chelate (**3**) by the dicarboxylate (see Scheme I). ^{195}Pt NMR spectroscopy is rather inconvenient for the detection of the unidentate adduct (**2**), since the difference in chemical shifts between the diaqua and the monocarboxylate monoaqua species is small and the line widths of the platinum resonances are broad. We expected to monitor the disappearance of the single peak of the symmetric diaqua complex (**1**) (by ^{15}N NMR spectroscopy) and the growing of the nonsymmetric complex (**2**). In practice, no peaks that could be assigned to species **2** appeared, but instead we observed the resonances of **3** shortly after the reaction had begun. The rapid formation of **3** is attributed to the electrostatic attraction between the negatively charged carboxylate and the positively charged platinum ion, which leads to the fast ring closure to give the O,O chelate. The ^{15}N spectrum (see Figure 2) of the thermodynamic product displayed two resonances at 64.07 and 83.66 ppm. The former belongs to the amine trans to the nitrogen donor (NH_2 group of amal) and the latter to the amine that is trans to the coordinated carboxylate group. These data further support the assignment of the N,O chelation, which has been based on ^{195}Pt NMR spectroscopy. A dicarboxylate complex would have yielded a single resonance in the ^{15}N NMR spectrum owing to the magnetic equivalence of the two amine groups.

In the ^{13}C NMR spectrum of compound **4** we observed two distinct carbonyl resonances (at 171.52 and 186.30 ppm). Since malonic acid has a single resonance at 171.57 ppm,[33] we conclude that the resonance at 186.30 ppm belongs to the coordinated carboxyl, while the one at 171.52 ppm corresponds to the free carboxyl. A similar assignment has been made by Appleton et al.[29] for the Pt complex of methyliminodiacetate. The long recycle delays needed for the detection of the carbonyl resonances (which are not relaxed by adjacent protons) render this technique unfavorable for kinetic measurements.

One of the reviewers suggested that decarboxylation of the aminomalonate complexes might occur. At his suggestion we measured the ^{13}C NMR spectrum of the original bis(cyclobutylamine) aminomalonate complex previously described[20] and observed two resonances in the carbonyl region at 171.3 and 185.8 ppm. This, in conjunction with the ^{13}C NMR spectrum of the diammine complex (see above) and the analytical results previously reported,[20] indicates that in our hands, under the conditions specified, we did not observe any decarboxylation.

We have carefully examined the ^{195}Pt NMR spectra of all the aminomalonate complexes searching for possible hydroxy-bridged

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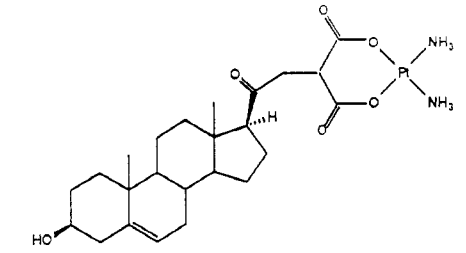

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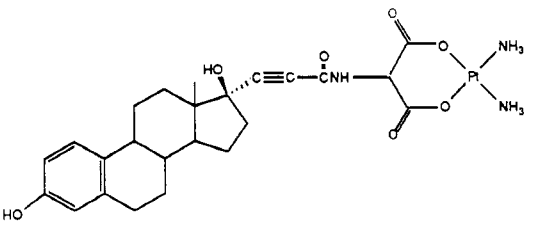

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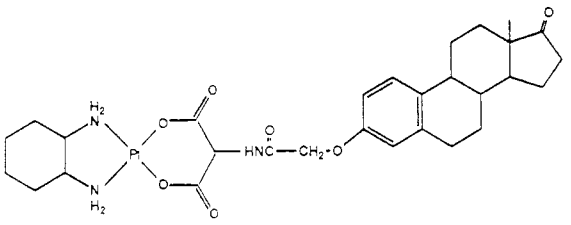

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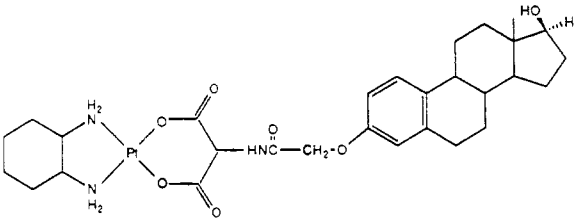

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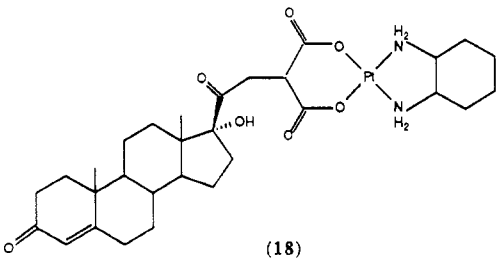

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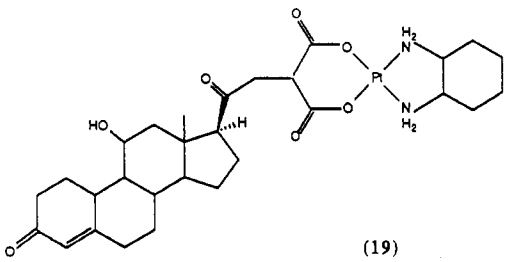


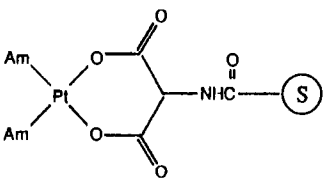
(19)

Figure 3. Labeling scheme for the platinum diamine complexes of the steroidal hormones.

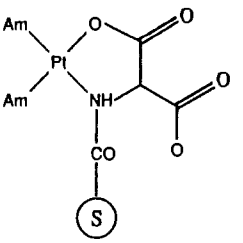
Table II. ^{195}Pt Chemical Shifts and Product Distribution for Selected Pt–Steroid Complexes

compd no.[a]	−δ, ppm O,O	−δ, ppm N,O	prod dist O,O:N,O ratio
14	1747		
15	1735	2022	3:2
16	1938, 1950[b]	2235, 2253[b]	4:1
17	1933, 1946[b]	2230, 2248[b]	5:1
18	1930, 1944[b]		
19	1935, 1950[b]		

[a] For detailed structures, see Figure 3. [b] The two signals result from a mixture of the DACH isomers.



(20)
O,O - Chelate



(21)
N,O - Chelate

Figure 4. Products of the reaction between $[Pt(Am_2]^{2+}$ and (a, left) compound **14** and (b, right) compound **15**.

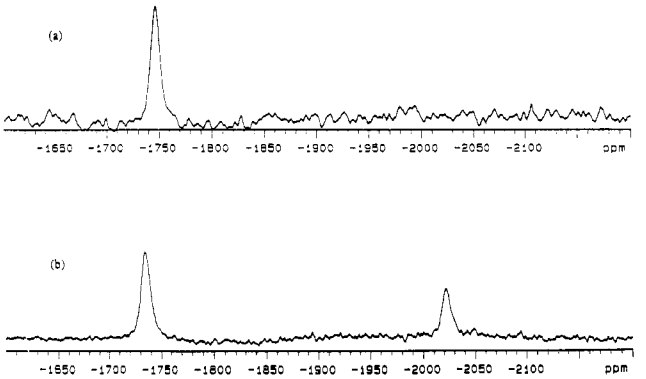


Figure 5. ^{195}Pt NMR spectra of (a) compound **14** and (b) compound **15**.

dimers or chloro complexes, which have been suggested as possible active impurities.[18,27] We have found no evidence for the existence of either species.

Complexes of Steroidal Hormones. We have sampled some of the $PtAm_2$ complexes that we had previously tethered to steroidal hormones and measured their ^{195}Pt NMR spectra (compounds **14–19**). The labeling scheme appears in Figure 3, and the NMR results appear in Table II. We could distinguish between complexes that contained an amide group with a nitrogen atom at an α position relative to the dicarboxylate unit and those that did not. Under the reaction conditions used for the complexation reaction, the ligands containing an amide linkage (compounds **15–17**) gave rise to a mixture of isomers whereas those lacking the amide group (**14**, **18**, **19**) gave rise to a single isomer (see Figure 4). Compounds **15–17** display resonances at the −1700 to −1900 ppm range (assigned to the dicarboxylate complex (**20**)) and at the −2100 to −2300 ppm (indicative of N,O chelation through the amide linkage (**21**)). Table II and Figure 5 indicate that the ratio between the O,O chelate and the N,O chelate is in favor of the former. It is possible that under different reaction conditions (e.g. higher temperatures and longer reaction periods) a different isomeric ratio favoring the N,O chelate (which we believe is the thermodynamic product) could probably be obtained. Compounds **14**, **18**, and **19** exhibited resonances only in the chemical shift region that corresponds to the O,O chelate (the two resonances observed for the DACH complexes are assigned

to the two isomers of the DACH ligand). The low solubility of these compounds made further separations and purifications extremely difficult.

Conclusions

In this study we have shown that the initial product formed upon reaction between diaminediaquaplatinum(II) complexes and aminomalonate is the O,O chelate $[PtAm_2(amal\text{-}O,O)]^+$. As the reaction progresses, the kinetic product isomerizes to give the thermodynamically stable $PtAm_2(amal\text{-}N,O)$. The inertness of the Pt–N bond is responsible for the formation and for the stability of the thermodynamic products.

Registry No. **1**, 20115-64-4; **3**, 129365-85-1; **4**, 129365-87-3; **5**, 129965-00-0; **6**, 129965-01-1; **7**, 129964-99-4; **8**, 129965-02-2; **9**, 129965-03-3; **10**, 129965-04-4; **12**, 129965-05-5; **13**, 129965-06-6; **14**, 121858-78-4; **15** (O,O isomer), 125445-71-8; **15** (N,O isomer), 129965-08-8; **16** (O,O isomer), 121857-22-5; **16** (N,O isomer), 129965-09-9; **17** (O,O isomer), 121864-98-0; **17** (N,O isomer), 129965-10-2; **18**, 121857-31-6; **19**, 129965-07-7; ^{195}Pt, 14191-88-9; $Pt(NH_3)_2(SO_4)(H_2O)$, 86493-49-4.

Notes

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Mesomorphic Properties of Metallonematogens, Bis[4-((4-alkoxybenzoyl)oxy)-*N*-(*n*-alkyl)salicylaldiminato]copper(II) Complexes

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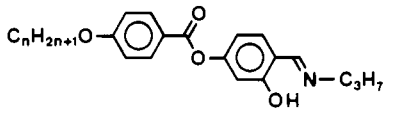
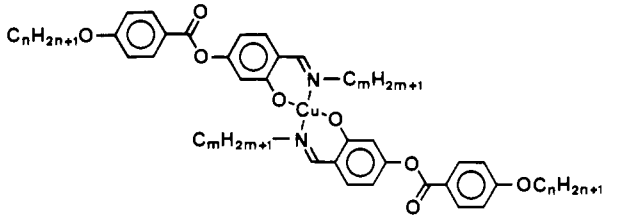
Introduction

We have previously reported a synthetic and structural study on a homologous series of liquid crystalline copper(II) complexes of *N*-salicylideneaniline derivatives, which exhibit both nematic and smectic C phases.[1] As an extension of this work, we have replaced the *N*-phenyl moieties by *N*-alkyl groups in the hope of obtaining the nematic phase over a manageable temperature range and prepared homologous series of 3-hydroxy-4-((propylimino)-methyl)phenyl 4-alkoxybenzoates (LA) and copper(II) complexes having various terminal and lateral alkyl chains, bis[4-((4-alkoxybenzoyl)oxy)-*N*-(*n*-propyl)salicylaldiminato]copper(II) ($Cu(LA)_2$) and bis[4-((4-(hexyloxy)benzoyl)oxy)-*N*-(*n*-alkyl)-salicylaldiminato]copper(II) ($Cu(LB)_2$), respectively. The terms



LA; n=4–12, 14, 16, 18



$Cu(LA)_2$; m=3, n=4–12, 14, 16, 18

$Cu(LB)_2$; n=6, m=1, 2, 4–13

terminal and lateral are based on a view that the bis(4-(benzoyloxy)salicylaldiminato)copper core constitutes a rigid core part of this mesogenic molecule. All of the compounds proved to show the nematic phases.

Results and Discussion

The phase behavior was studied by polarizing microscopic observation and by differential scanning calorimetry. Table I

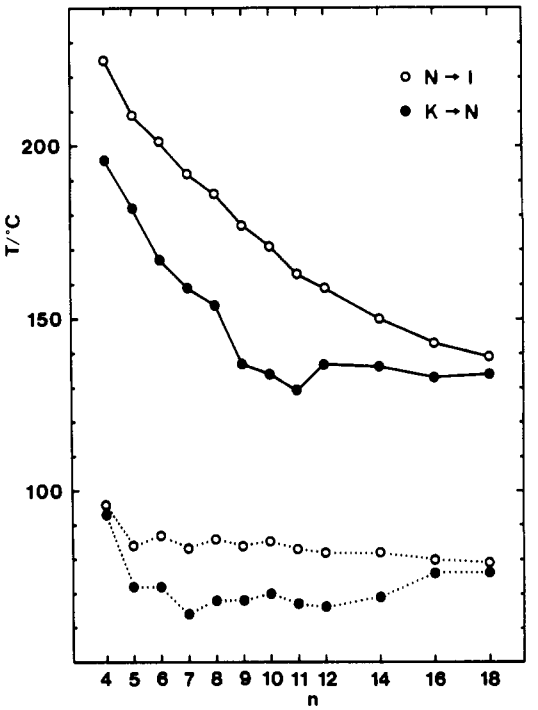


Figure 1. Plots of mesomorphic transition temperatures vs terminal alkyl chain length (*n*) for LA (dotted line) and $Cu(LA)_2$ (solid line).

summarizes the mesomorphic transition temperatures and enthalpy changes determined by the latter means for the homologous series of LA, $Cu(LA)_2$, and $Cu(LB)_2$. Here K,[2] N, and I denote crystalline, nematic, and isotropic phases, respectively, and each homologue is designated by the number of carbon atoms in the terminal alkyl chains, *n*, for LA and $Cu(LA)_2$, and in the lateral alkyl groups, *m*, for $Cu(LB)_2$.

Mesomorphic Properties of LA and $Cu(LA)_2$. Figure 1 gives a graphic comparison of phase behaviors of LA and $Cu(LA)_2$. It is seen that all of the ligand homologues exhibit enantiotropic nematic phases, though only over narrow temperature ranges. The phases were characterized by their marble textures under a crossed polarizing microscope, and the magnitude of isotropization enthalpies also supports the identification.[3] The mesomorphic property of 4-((propylimino)methyl)phenyl 4-(pentyloxy)benzoate, a two-ring compound analogous to LA ($n = 5$) but lacking the 3-hydroxyl group, has been reported by Weissflog et al.[4] to show

(1) Hoshino, N.; Murakami, H.; Matsunaga, Y.; Inabe, T.; Maruyama, Y. *Inorg. Chem.* **1990**, *29*(6), 1177–1181.

(2) Melting points and enthalpies were determined also with annealed specimens whenever the presence of lower melting metastable forms in virgin crystals was indicated by solid–solid transition peaks and/or double melting behavior on DSC thermograms.

(3) Demus, D.; Diele, S.; Grande, S.; Sackmann, H. In *Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic Press: New York, 1983; Vol. 6, pp 1–107.

(4) Weissflog, W.; Möckel, P.; Tschimeg, Sh.; Kresse, H.; Demus, D. *J. Prakt. Chem.* **1981**, *323* (4), 599–606.

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