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PHOTOCHEMISTRY AND CHARGE TRANSFER CHEMISTRY OF THE PLATINUM GROUP ELEMENTS

Progress Report

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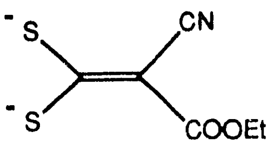
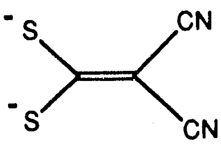
SUMMARY OF PROGRESS IN YEAR TWO

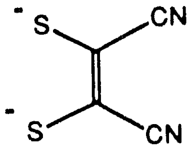
During Year 2 of the current grant period, significant progress was made on the photochemistry and photophysics of platinum group element dithiolate complexes. The specific systems under investigation are square planar complexes of Pt(II) containing a dithiolate chelate and two other donor groups to complete the coordination sphere. The donor groups may be amines, imines, phosphines, phosphites or olefins, and they can be either monodentate or joined together as part of a chelate ring. The dithiolate ligands used in these studies are primarily ecda, i-mnt and mnt, although other related ligand systems have been employed as a means of probing electronic structural features of the complexes and as a way of increasing solution solubility.



ecda



i-mnt



mnt

Prior to the current year, a series of diimine dithiolate complexes, where diimine = 2,2'-bipyridine (bpy), 1,10-phenanthroline (o-phen), dimethylbipyridine (Me_2bpy), diphenylbipyridine (Ph_2bpy) and diphenylphenanthroline (Ph_2phen), had been synthesized and found to luminesce in fluid solution. The complexes were also observed to be highly solvatochromic and exhibited electron transfer quenching of emission in the presence of either donors or acceptors.

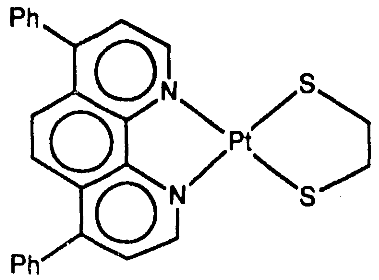
A key focus of the studies over the last two years has been elucidation of the electronic structures of these complexes with particular emphasis on understanding the nature of their excited states and the basis of their solvatochromism. During the past year, one phase of the studies has neared completion with the preparation and submission of three manuscripts presently under review and a presentation of this work at the 9th International Symposium on the Photochemistry and Photophysics of Coordination Compounds in Fribourg, Switzerland last July.[1]

Through systematic ligand variation in which the unsaturated dithiolate was replaced with a saturated dithiolate, bis(thiolates), bis(selenolates) and chlorides and the diimine was replaced with di(phosphines), diolefins and the saturated ligand cyclohexanediamine, we found that the solvatochromic band originates from a transition between an orbital that has Pt d and S p character to a π^* orbital of the diimine ligand. This conclusion is supported by extended Huckel molecular orbital calculations and by electrochemistry. Figure 1 presents the HOMO and LUMO orbitals of the complexes Pt(bpy)(i-mnt) and Pt(bpy)(mnt). Cyclic voltammetry shows that: (1) the diimine complexes reduce at much less negative potentials than the corresponding di(phosphine) derivatives indicating that the LUMO is π^*(diimine)-based and (2) the complexes undergo irreversible oxidation at less forcing potentials than needed for coordinated phosphine or diimine oxidation consistent with a metal-dithiolate HOMO.

Studies of the temperature dependence of the emission of Pt(Me_2bpy)(ecda), Pt(Ph_2phen)(ecda) and Pt(Ph_2phen)(mnt) were previously described. The key conclusions were: (1) a single emission occurs from the mnt complex showing simple exponential decay and considerable vibronic structure, leading to an excited state assignment of ^{3}(d-π^*(mnt)); (2) the ecda complexes show emission from several different emitting states; (3) one of these states, which is only observed below 100K, is a $^3(\pi\pi^*)$ state of the chelated diimine; and (4) the other state is of ^{3}(Pt(d)/S(p)-π^*(diimine)) origin with spin-orbit split components.

A simple energy level diagram for the diimine dithiolate complexes based on the EHMO calculations is shown in Figure 2 along with the energy levels of $PtCl_4^{2-}$ and Pt(bpy)Cl_2 presented on a relative basis. The key factor in determining the different emission characteristics of the mnt and ecda complexes is where the first π^*(dithiolate) level is located relative to the π^*(diimine) LUMO. For mnt complexes, these two levels are nearly of same energy and emission originates from the triplet state involving π^*(mnt). For the ecda complexes, the π^*(dithiolate) level is much higher in energy and the emitting state involves the π^*(diimine) level.

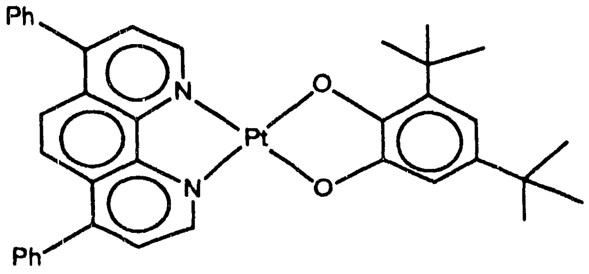
In the course of carrying out systematic ligand variation, two interesting observations were noted. First, the saturated dithiolate complex $Pt(Ph_2phen)(edt)$ shown below was



$Pt(Ph_2phen)(edt)$

observed to bleach in the presence of air when exposed to light. Second, the O-donor complex $Pt(Ph_2phen)(O_2C_6H_2(t\text{-}Bu)_2)$ was prepared and found to have a solvatochromic shift larger than any of the dithiolate systems.

The first observation is suggestive of a photochemical reaction involving the excited complex and O_2, leading to either $^1O_2$ or O_2^- formation. We will determine if $^1O_2$ formation is generated on photolysis of $Pt(Ph_2phen)(edt)$ and whether more stable analogs can be used for promoting oxidation reactions such as allylic oxidation. The second observation involving $Pt(Ph_2(phen)(O_2C_6H_2(t\text{-}Bu)_2)$ and related catecholate systems requires a reexamination of the

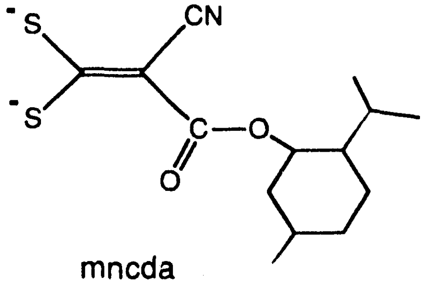


$Pt(Ph_2phen)(O_2C_6H_2(t\text{-}Bu)_2)$

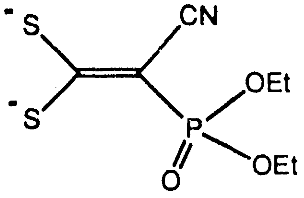
solvatochromic transition and in particular the nature of the highest occupied molecular orbital in these complexes. The notion that the solvent-dependent transition in these systems corresponds, at least partly, to an interligand charge transfer band which is necessarily directional in a square planar complex makes these systems of some interest in terms of their dipole moments, polarizabilities and nonlinear optical responses.

Another unexpected result during the year was the observation that the complex $Pt(tbcda)_2^{2-}$ (tbcda is the t-butyl analog of ecda) is emissive in the solid state at 77K. Prior to this result the only bis(dithiolate) complex of Pt(II) found to emit was Pt(mnt)$_2^{2-}$.[2] Further studies have shown emission from related bis dithiolates such as Pt(i-mnt)$_2^{2-}$ and give evidence of two emitting states (see Figure 3). The complex Pt(i-mnt)$_2^{2-}$ is also found to undergo a photoreaction in CHCl$_3$ upon irradiation at 300-400 nm. The products of this photolysis are under investigation, but the reaction is clean as evidenced by Figure 4.

Other progress during the year involved continued characterization of the phosphine and diolefin complexes of Pt(II) containing ecda and the preparation of new ligand systems. With regard to the former, the structures of Pt(dppe)(mnt) and Pt(dppb)(mnt) were determined by single crystal X-ray methods (see Figure 5) and the ^{31}P-NMR spectra proved to be interesting. The spectra show an AB pattern for the phosphine donors that changes in the ^{195}Pt satellites as a consequence of two different J_{PtP}'s for a given $\Delta\delta$ and J_{PP}. This is illustrated in Figure 6. Complexes of the new ligand systems mncda and epcda were also prepared.



mncda



epcda

During the coming year, efforts will focus on the photochemistry of these complexes including the photobleaching of Pt(Ph$_2$phen)(edt) and on the photolysis of Pt(tbcda)$_2^{2-}$. Efforts will also be made on the photoreduction capabilities of these complexes and a determination of excited state potentials.

References

1. (a) Zuleta, J. A.; Bevilacqua, J. M.; Rehm, J. M.; Eisenberg, R. *Inorg. Chem.* **1992**, in press; (b) Zuleta, J. A.; Bevilacqua, J. M.; Prosperpio, D. M.; Eisenberg, R. *J. Am. Chem. Soc.* **1991**, submitted for publication; (c) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1992**, in press.
2. Gunter, W.; Gliemann, G.; Klement, U.; Zabel, M. *Inorg. Chim. Acta* **1989**, *165*, 51.

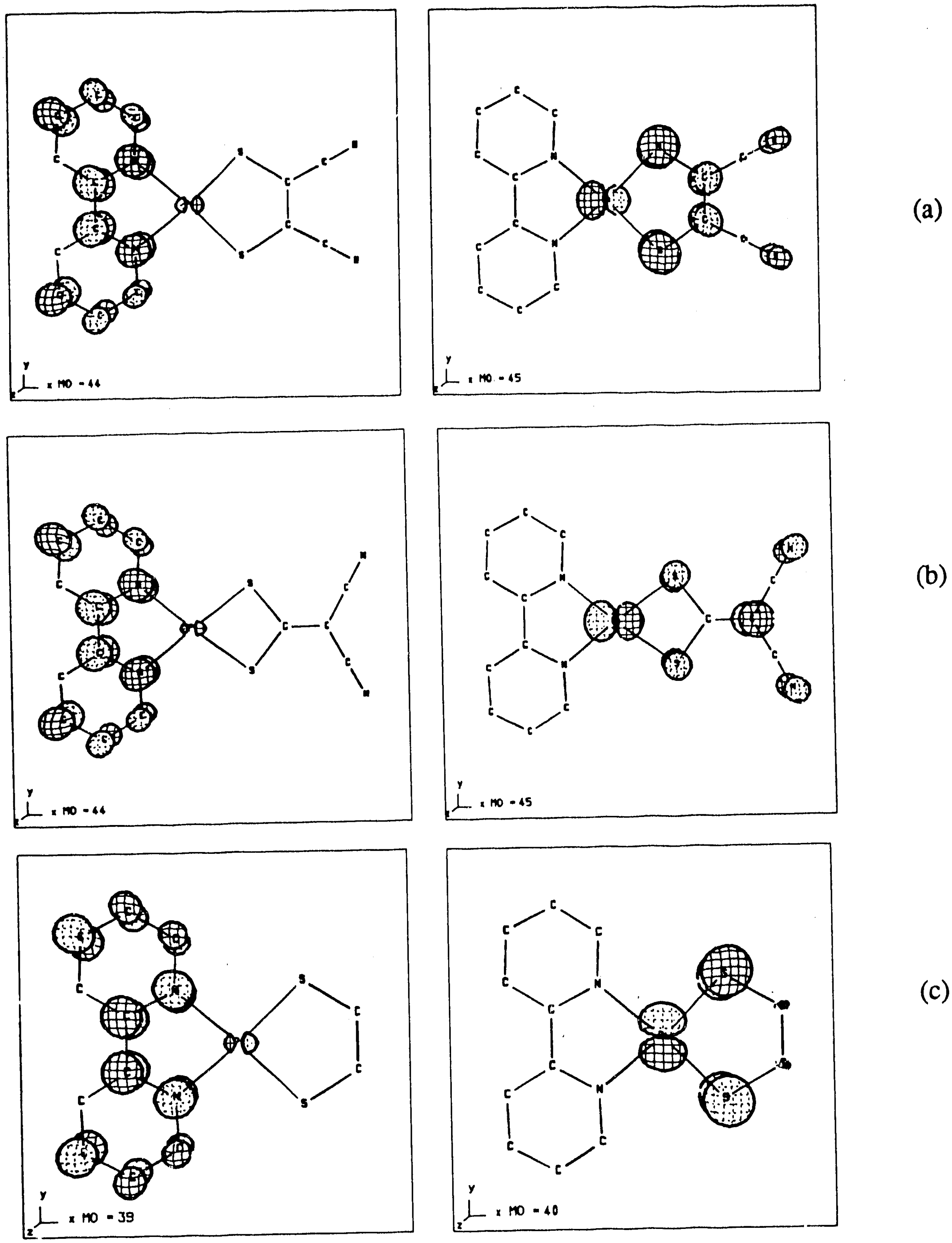


Figure 1. Highest occupied (right) and lowest unoccupied molecular orbitals of (a) Pt(bpy)(mnt), (b) Pt(bpy)(i-mnt) and (c) Pt(bpy)(SCH_2CH_2S).

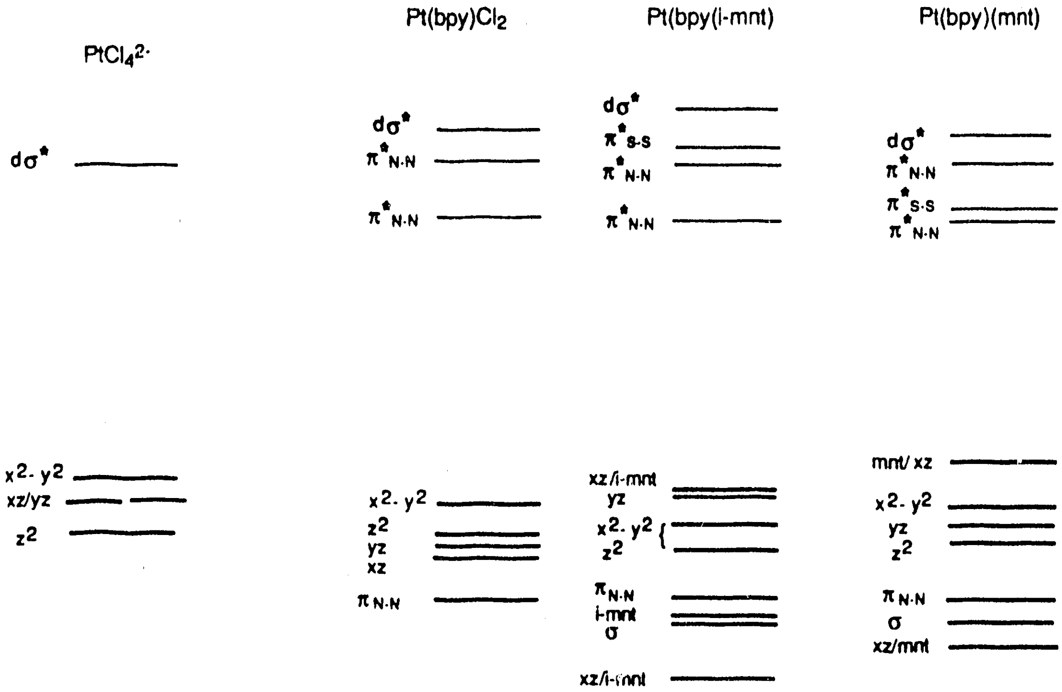


Figure 2. Energy level orderings for square planar complexes.

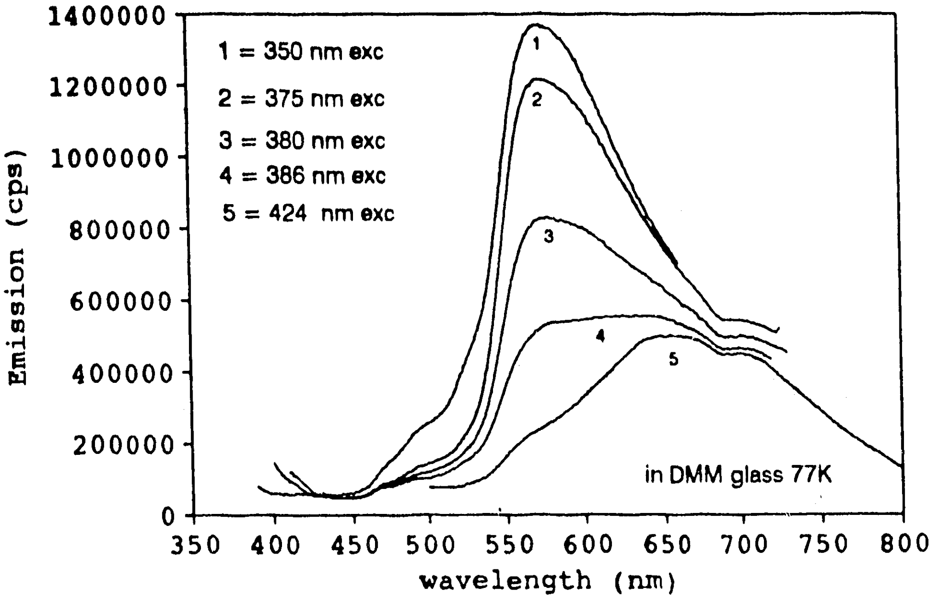


Figure 3. Emission from Pt(i-mnt)$_2{}^{2-}$ dependent on excitation position.

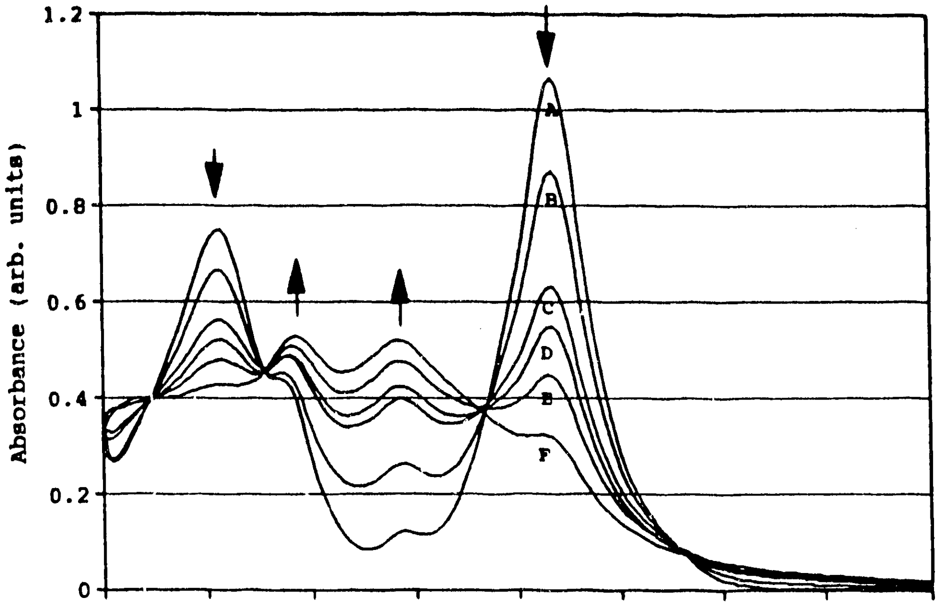


Figure 4. Photolysis of TBA[Pt(i-mnt)$_2$] with 300 nm $<\lambda<$ 400 nm. (A) 0 min. (B) 80 min. (C) 180 min. (D) 230 min. (E) 295 min. (F) 420 min.

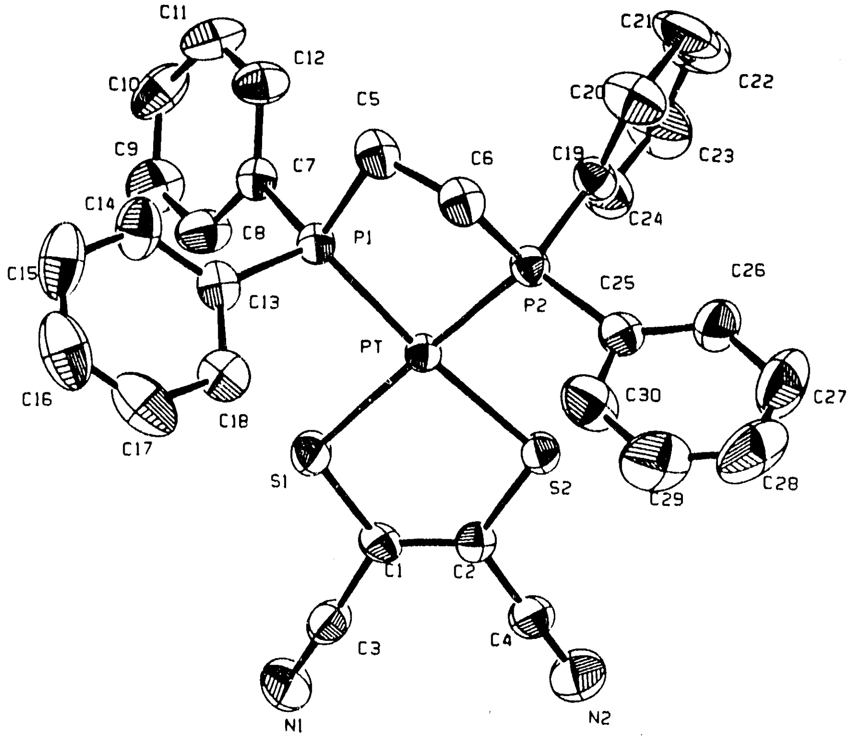


Figure 5. Molecular structure of Pt(dppe)(mnt).

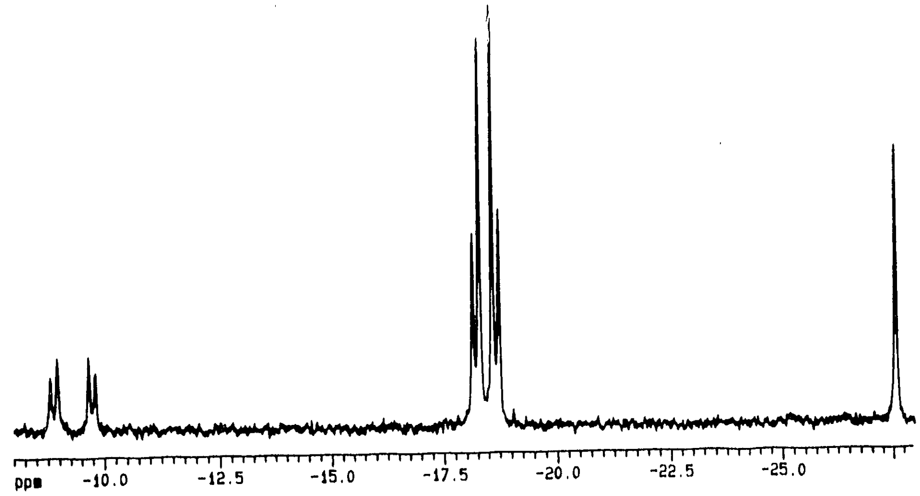


Figure 6. $^{31}P\{^1H\}$ NMR spectrum of $Pt(PMe_2Ph)_2(ecda)$.

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