Inorg. Chem. **2002**, *41*, 4531–4538

Inorganic Chemistry Article

Chromium Complexes of an Isomeric *N*-Donor Ligand, 2-[(*N*-Arylamino)phenylazo]pyridine: Amination Reactions, X-ray Structure, and Redox Properties

Kunal K. Kamar,[†] Amrita Saha,[†] Alfonso Castiñeiras,[‡] Chen-Hsiung Hung,[§] and Sreebrata Goswami*,[†]

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Kolkata 700 032, India, Departamento de Quimica Inorganica, Universidade de Santiago de
Compostela, Campus Universitario Sur, E-15782 Santiago de Compostela, Spain, and
Department of Chemistry, National Changhua University of Education,
Changhua, Taiwan 500, Republic of China

Received February 25, 2002

The chromium chemistry of two positional isomers of the ligand 2-[(*N*-arylamino)phenylazo]pyridine ($HL^1$and HL^2) are described. While the ligand HL^1 coordinates as a bischelating tridentate *N*,*N*,*N*-donor, $[L^1]^-$, with deprotonation of the amine nitrogen, its isomer HL^2 coordinates as a neutral bidentate *N*,*N*-donor. The amine nitrogen in this case remains protonated. Thus the reaction of $CrCl_3 \cdot nH_2O$ with HL^1 produced the brown cationic complex, $[Cr(L^1)_2]^+$, [**1**]$^+$. The representative X-ray structure of [**1a**](ClO$_4$) is reported. The two azo nitrogens of the anioinc tridentate ligand approach the metal center closest with Cr(1)–N(azo) av 1.862(6) Å. There is a significant degree of ligand backbone conjugation in the coordinated ligands, which resulted in shortening of the C–N distances and also in lengthening of the diazo (N═N) distances. Two synthetic approaches for the synthesis of chromium complexes of HL^2 are investigated. The first approach is based on the substitution reaction, wherein all the coordinated CO ligands of $Cr(CO)_6$ were completely substituted by the three bidentate HL^2 ligands to produce a violet complex $[Cr(HL^2)_3]$. The second approach is based on para-amination reaction of coordinated 2-(phenylazo)pyridine (pap). Thus the reaction of an inert complex, $[CrCl_2(pap)_2]$, with $ArNH_2$ yields a mixed ligand complex, $[CrCl_2(pap)(HL^2)]$, **3**. In this reaction one of the two coordinated pap ligands in $[CrCl_2(pap)_2]$ undergoes amination at the para carbon (with respect to the diazo function) to yield HL^2 in situ. This metal-promoted transformation is authenticated by the X-ray structure determination of a representative complex, $[CrCl_2(pap)(HL^{2a})]$, **3a**. Notable differences in bond distances along the ligand backbones of the two coordinated ligands in **3a** indicate different levels of metal–ligand overlap in this complex. All the chromium complexes of HL^2 are characterized by their intense blue-violet color. The frequencies of the visible range transitions in these complexes linearly correlate with the Hammett's substitution constant. Intraligand charge-transfer transitions in the visible region are believed to be responsible for the intense color. Redox properties of all these complexes are reported.

Introduction

In recent years we have been interested[1−5] in the coordination chemistry of the 2-[(*N*-arylamino)phenylazo]pyridine ligand. Two positional isomers of this ligand, viz., HL^1 and HL^2, were isolated by us by metal-promoted aromatic ring amination reactions of the coordinated 2-(phenylazo)pyridine ligand (pap) (Chart 1). The amination reaction is regioselective, occurring at ortho and para carbons in the presence of a labile and inert metal complex mediator, respectively. While the ortho-aminated ligand HL^1 can act as a monoanionic tridentate *N*,*N*,*N*-donor with the dissociation of the

---

* Address correspondence to this author. E-mail: icsg@mahendra.iacs.res.in.

[†] Indian Association for the Cultivation of Science.

[‡] Universidade de Santiago de Compostela.

[§] National Changhua University of Education.

(1) Saha, A.; Ghosh, A. K.; Majumdar, P.; Mitra, K. N.; Mondal, S.; Rajak, K. K.; Falvello, L. R.; Goswami, S. *Organometallics* **1999**, *18*, 3772.

(2) Ghosh, A. K.; Majumdar, P.; Falvello, L. R.; Mustafa, G.; Goswami, S. *Organometallics* **1999**, *18*, 5086.

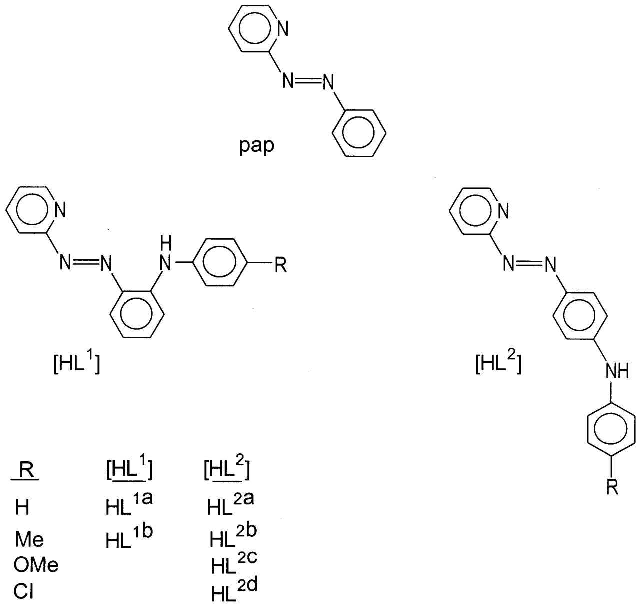
(3) Saha, A.; Majumdar, P.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **2000**, 1703.

(4) Saha, A.; Majumdar, P.; Peng, S.-M.; Goswami, S. *Eur. J. Inorg. Chem.* **2000**, 2631.

(5) Das, C.; Peng. S.-M.; Lee, G.-H.; Goswami, S. *New J. Chem.* **2002**, *26*, 222.

10.1021/ic0201497 CCC: $22.00

Chart 1



R	[HL^1]	[HL^2]
H	HL^{1a}	HL^{2a}
Me	HL^{1b}	HL^{2b}
OMe		HL^{2c}
Cl		HL^{2d}

amine proton, the para-aminated ligand, HL^2, coordinates as a neutral *N*,*N*-donor. The deprotonated anionic ligand [L^1]$^-$ has a unique combination of a strong acceptor[6] azopyridine group (soft) and a strong electron donor[7] amido function (hard), which act in concert in the stabilization of variable valence states of metal ions in the complexes. Thus the iron complex [Fe(L^1)$_2$]$^{n+}$ was isolated[4] both as a cationic [Fe^{III}(L^1)$_2$]$^+$ and a molecular [Fe^{II}(L^1)$_2$] complex. Moreover, this ligand is known to stabilize uncommon low-spin states[3,4] of metal ions, some examples being Mn(II) (t$_2{}^5$), Fe(II) (t$_2{}^6$), and Fe(III) (t$_2{}^5$). Extensive charge delocalization of [L^1]$^-$ along the ligand backbone in its complexes was also noted. The neutral bidentate ligand, HL^2, on the other hand, uses[1] the pyridine(N) and the diazo(N) for coordination, the amine(N) remaining protonated and uncoordinated, which may act as a potential donor in a charge-transfer transition. Notably, the azopyridine function[6] of HL^2 is known to be an acceptor chromophore—a property that is expected to be augmented upon coordination to a metal ion (Lewis acid). So, intraligand charge transfer in the metal complexes of HL^2 may be observed in the low-energy visible region. We wish to note here that complexes of such types of ligands having both donor and acceptor chromophores are of recent interest in the context of synthesis of octupolar molecules[8] for the study of nonlinear optical properties.

Herein we describe the synthesis and properties of a series of chromium(II) and chromium(III) complexes of the isomeric 2-[(*N*-arylamino)phenylazo]pyridine ligands. Optical properties of these are markedly different than those of the parent chromium−pap complexes,[9−11] which are highlighted in this paper.

Results and Discussion

Synthesis. Two synthetic approaches were explored for the preparation of the chromium complexes. The first one was based on the reaction of preformed HL^1 and HL^2 ligands with the suitable starting chromium salt or its complex. We also have examined the amination reaction of coordinated 2-(phenylazo)pyridine in the two chromium complexes, viz., [CrCl$_2$(pap)$_2$] and [Cr(pap)$_3$](ClO$_4$), respectively. The above compounds were reported[9,11] and were shown to be substitutionally inert.

The complex [Cr(L^1)$_2$](ClO$_4$), [**1**](ClO$_4$), was obtained by heating chromium(III) chloride and the deprotonated ligand [L^1]$^-$ in a 1:2 molar proportion in absolute ethanol. The reaction mixture became redish brown in 2 h. The crude mass, so formed, was a mixture of a major red brown and several minor byproducts of different colors, which were observed on a TLC plate. The cationic complex, [Cr(L^1)$_2$]$^+$, [**1**]$^+$, was purified by using the preparative TLC technique and was finally isolated as its perchlorate salt in a moderate yield. The rest of the minor bands on the TLC plate were overlapping and we have not been successful in isolating them in the pure state. The reaction of HL^2 with Cr(CO)$_6$ led to complete substiution[10] of CO ligands from Cr(CO)$_6$ to produce the violet compound [Cr(HL^2)$_3$], **2** in 30% yield. Compound **2** was purified by rapid crystallization. The solution is not very stable and dissociates HL^2. The yields of the products from the above reactions are moderate to low. The several byproducts along with [**1**]$^+$ may have originated from the partial substitution of the inert CrCl$_3$ or be due to the deamination reaction of HL^1. The formation of multiple products from the reaction of [OsBr$_6$]$^{2-}$ and HL^1 was noted recently by us.[5] However, the major product from each of the above reactions was thoroughly purified either on a preparative TLC plate or by repeated crystallization. All these compounds gave consistent elemental analysis. Notably, while the ligand HL^1 coordinates as a bischelating tridentate ligand with deprotonation of the amine nitrogen, its isomer HL^2 coordinates as a neutral bidentate *N*,*N*-donor. The amine nitrogen in this case remains protonated.

To examine the amination reaction of coordinated 2-(phenylazo)pyridine using a chromium complex mediator, we chose the dichloro complex [CrCl$_2$(pap)$_2$] as the reactant. Since the chosen complex is known to be substitutionally inert, amination at the para carbon of the pendant phenyl ring was anticipated.[1] In line with our strategy the brown [CrCl$_2$(pap)$_2$] complex was reacted with neat ArNH$_2$ in air, which produced an intense blue mixture in 4 h. The usual workup followed by chromatographic purification of the mixture yielded crystalline complex [CrCl$_2$(pap)(HL^2)] in 30−40% yield. In this reaction one of the two coordinated pap ligands has undergone amination at the para carbon of the pendant phenyl group of a coordinated pap ligand. Notably, the amination reaction is regioselective and has occurred only at the para position. This is not unexpected, since it has already been shown that the availibility of vacant

---

(6) Goswami, S.; Mukherjee, R.; Chakravorty, A. *Inorg. Chem.* **1983**, 22, 2825.

(7) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.

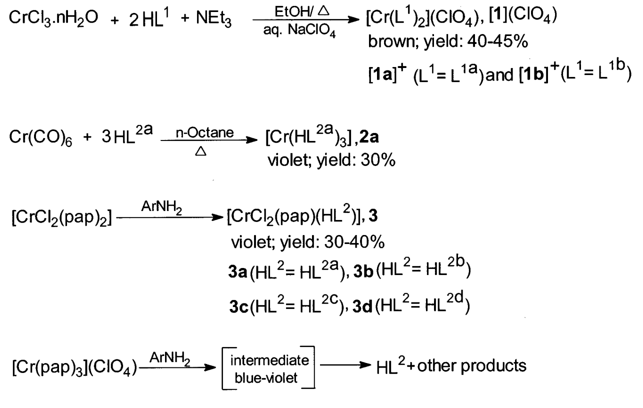
(8) Bozec, H. L.; Renouard, T. *Eur. J. Inorg. Chem.* **2000**, 229.

(9) Ferreira, V.; Krause, R. A. *Inorg. Chim. Acta* **1988**, *145*, 29.

(10) Ackermann, M. N.; Barton, C. R.; Deodene, C. J.; Specht, E. M.; Keill, S. C.; Schreiber, W. E.; Kim, H. *Inorg. Chem.* **1989**, *28*, 397.

(11) Kharmawphlang, W.; Choudhury, S.; Deb, A. K.; Goswami, S. *Inorg. Chem.* **1995**, *34*, 3828.

Scheme 1. Synthesis of Chromium Complexes



or labile coordination site(s) at the metal center of the mediator complex is an essential prerequisite for the ortho-amination reaction. In the present case there was no dissociation of coordinated ligand(s) during the course of the reaction and hence amination occurred only at a para position. Moreover, we wish to note here that the amination reaction at $[CrCl_2(pap)_2]$ is sluggish and occurs only partially (at one pap out of two). By contrast, similar type of reactions[1,4] with cationic mediator complexes such as $[Co(pap)_3]^{2+}$ and $[Fe(pap)_3]^{2+}$ are more facile and complete. Cationic complexes are more electrophilic and appear to be better mediators for the reaction. This proposal was further strengthened[12] by the fact that the molecular complex $[RuCl_2(pap)_2]$ is totally unreactive to $ArNH_2$, whereas the trischelate, $[Ru(pap)_3](ClO_4)_2$, is susceptible to amination. A similar amination reaction with the trischelate $[Cr(pap)_3](ClO_4)$ as the mediator complex and aniline as the reagent also produced a blue-violet mixture. Unfortunately, the crude product in this case could not be purified. This decomposes rapidly in solution and gives inconsistent analysis. The organic ligand that was isolated from the crude mixture was charaterized and found[4] to be the para-aminated ligand HL^{2a}. The synthetic reactions are summarized in Scheme 1. The above amination reactions occur only in neat aromatic amines and in the presence of air. The reaction conditions are not favorable for a mechanistic study. However, the site selectivity of this reaction depending on the nature of the mediator complex has been established beyond doubt.

X-ray Structure. Figures 1 and 2 show the ORTEP and atom numbering schemes for $[Cr(L^{1a})_2](ClO_4)$ and $[CrCl_2(pap)(HL^{2a})]$, respectively. The structural analysis of cationic $[Cr(L^{1a})_2]^+$ reveals the presence of two ligands, each of which acts as a *N*,*N*,*N*-tridentate donor with deprotonation of the amine nitrogens, viz. N(1) and N(5). The relative orientations within the pairs of identical coordinating N-atoms of the two ligands are cis, trans, and cis in the sequence of pyridyl-N, azo-N, and amido-N atoms. The chelate bite angles (N)py−Cr(1)−N(azo), N(4)−Cr(1)−N(2), and N(8)−Cr(1)−N(6) [av 79.7(3)°] are smaller than the N(azo)−Cr(1)−N(amide) bite angles [av 81.6(3)°]. The two azo nitrogen atoms of the anionic tridentate ligands approach the metal center more closely [Cr(1)−N(2)/(6), av 1.862(6) Å] than the other four Cr(1)−N bonds. There is an indication of significant backbone conjugation in the coordinated anionic ligand. The ligand HL^1 is a low-melting solid, and its X-ray quality crystals could not be developed so far. However, the X-ray structure of its isomer HL^2 is reported.[4] The average N−N azo distances [1.301(7) Å] in this complex are longer than that in HL^{2a} [1.264(2) Å]. Moreover, the average N(azo)−C(phenyl) distance [1.384(8) Å] is shorter than that observed for the corresponding distance in HL.[2a] The amido nitrogen atom of $[L^{2a}]^-$ binds to the phenyl group of pap at a shorter distance [e.g. C(7)−N(1), 1.341(9) Å] than that observed in HL^{2a} [1.405(2) Å]. These are all in agreement with the proposal of strong electron delocalization along the ligand backbone in the coordinated $[L^1]^-$ anion. Similar effects were noted[1,3,4] in other complexes of $[L^1]^-$ involving other 3d-metal ions.

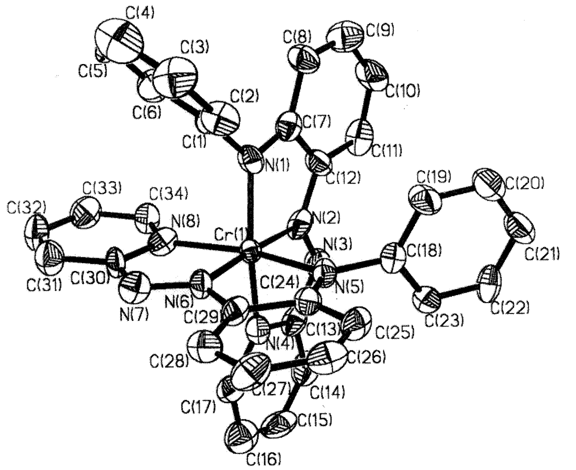


Figure 1. Molecular structure and atom numbering scheme for $[Cr(L^{1a})_2](ClO_4)$.

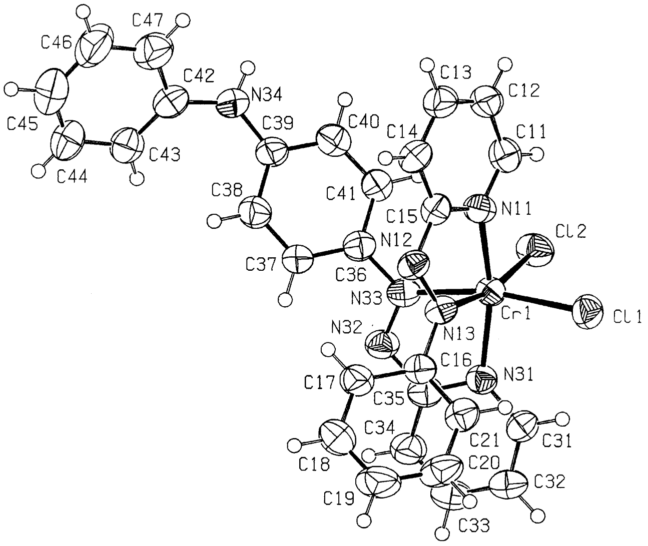


Figure 2. Molecular structure and atom numbering scheme for $[CrCl_2(pap)(HL^{2a})]$.

The structural analysis of **3a** indeed authenticated the fusion of $ArNH_2$ to one of the coordinated pap ligands of $[CrCl_2(pap)_2]$. In this complex, the chromium center is surrounded by a distorted octahedral coordination environ-

---

(12) Das, C.; Saha, A.; Goswami, S. Unpublished results.

ment of two chloride ligands, the bidentate chelating ligand, pap, and the extended neutral ligand, HL^{2a}, which contains N(31), N(33), and N(34). The extended ligand has the aniline fragment fused to the phenyl ring of coordinated pap at the para position (relative to the azo fragment). This ligand is a bidentate and chelates to chromium through the pyridine nitrogen N(31) and the azo nitrogen N(33). The amine nitrogen N(34) bears a hydrogen atom, which is in marked opposition to the coordination mode of the corresponding ortho isomer [L^1]$^-$. The ligand [L^1]$^-$ binds as an anionic tridentate *N,N,N*-donor as discussed before. The compound has the cis moiety. Isomer description of this may be described by considering the relative positions in the pair N(py), N(py) and in the pair N(azo), N(azo) taken in that order. Thus the geometry of complex **3a** is trans, cis, which is identical[9] with that of the starting dihalo [$CrCl_2(pap)_2$]. Hence the amination reaction is stereoretentive.

The chelate bite angle of pap, N(11)−Cr(1)−N(13), is 76.87(18)°, while the corresponding N(31)−Cr(1)−N(33) in the extended ligand is 75.72(17)°. However, notable differences in bond distances along the ligand backbones of the two coordinated ligands indicate different levels of metal−ligand overlap in this complex. In the complexes of pap ligands, N−N lengths has been used[13,14] as a marker for the assessment of the degree of metal(dπ)−azo(pπ) interactions. In the structure of **3a**, the N−N distance in the pap ligand, N(12)−N(13), is 1.325(5) Å, while the corresponding distance in the extended ligand HL^{2a}, N(32)−N(33), is considerably shorter, 1.287(6) Å. Moreover, the Cr(1)−N(13) length [1.972(4) Å] is much shorter than the corresponding Cr(1)−N(33) distance [2.084(4) Å]. In fact, the chromium−azo bond length in the extended ligand is longer even than the chromium−pyridyl bond lengths in the reference compound. This effect may be explained by considering the extended ligand as a *p*-N(H)Ph-sustituted pap ligand. The strong electron-donating effect of the substitution is responsible for the shortening of the N(34)−C(39) length [1.371(7) Å] as compared to the corresponding N(34)−C(42) length [1.406(7) Å]. The presence of the strongly donating −N(H)Ph substitution at the phenyl ring makes the ligand HL^{2a} a weaker acceptor than the unsubstituted pap ligand.

Optical Spectra. The ability of the azo ligands, under consideration, to act as π-acceptor toward low-valent metal ions is documented in the literature. A diagnostic test for the existence of the metal(dπ)−ligand(pπ) interaction is the lengthening of N−N lengths in their metal complexes and also the shift of $\nu_{N=N}$ to lower frequencies[13,14] in moving from the free ligands to their complexes. Notably, the $\nu_{N=N}$ in pap, HL^1, and HL^2 appear at 1425, 1380, and 1390 cm^{-1}, respectively. These value in the complexes are appreciably lowered (Table 2).

Table 1. Selected Bond Lengths and Bond Angles of [**1a**](ClO_4) and **3a**

[**1a**](ClO_4)		**3a**	
bond lengths (Å)			
Cr(1)−N(2)	1.853(6)	Cr(1)−N(11)	2.018(4)
Cr(1)−N(6)	1.872(6)	Cr(1)−N(13)	1.971(4)
Cr(1)−N(1)	1.908(6)	Cr(1)−N(31)	2.065(4)
Cr(1)−N(4)	1.928(6)	Cr(1)−N(33)	2.084(4)
Cr(1)−N(5)	1.929(5)	Cr(1)−Cl(1)	2.3285(16)
Cr(1)−N(8)	1.948(6)	Cr(1)−Cl(2)	2.3252(17)
N(8)−C(30)	1.369(9)	N(12)−N(13)	1.326(5)
N(7)−C(30)	1.355(9)	N(32)−N(33)	1.288(5)
N(6)−N(7)	1.296(7)	C(15)−N(12)	1.372(6)
N(6)−C(29)	1.386(8)	C(35)−N(32)	1.392(6)
C(29)−C(24)	1.406(9)	C(36)−N(33)	1.401(6)
N(5)−C(24)	1.371(8)	C(16)−N(13)	1.427(6)
N(5)−C(18)	1.432(8)		
bond angles (deg)			
N(2)−Cr(1)−N(1)	82.5(3)	N(11)−Cr(1)−N(13)	76.89(17)
N(6)−Cr(1)−N(5)	80.7(3)	N(31)−Cr(1)−N(33)	75.74(16)
N(2)−Cr(1)−N(4)	80.3(3)	Cl(1)−Cr(1)−Cl(2)	92.55(6)
N(6)−Cr(1)−N(8)	79.1(3)	C(39)−N(34)−C(42)	129.8(5)

The solution spectral data of the complexes are collected in Table 2. Unlike other chromium complexes[11] of *N*-donor ligands, the parent complexes in solutions exhibit intense color. For example, the color of the Cr(III) complex, [Cr(L^1)$_2$]$^+$, is red-brown and is characterized by highly intense visible range transitions. As noted before[4] the molecular orbitals that are involved in the low-energy transitions of the metal complexes of [L^1]$^-$ are highly delocalized. Strong delocalization in the present chromium(III) complex is also obvious from its crystallographic data. Intense low-energy transitions may thus be due to $\pi-\pi^*$ transitions. Two more weak transitions in the near-IR region of these chromium(III) complexes were also noted. The color of the chromium complexes containing the HL^2 ligand, [$CrCl_2$(pap)(HL^2)], is intense blue-violet in dichloromethane. Notably, the color of the corresponding complex, [$CrCl_2(pap)_2$], is brown[9] in the same solvent. The spectra of the above two dichloro complexes are displayed for comparison (Figure 4). The additional highly intense visible range transition near 565 nm (ϵ, 20800 mol^{-1}cm^{-1}) in **3a** is no doubt responsible for the intense solution color of these compounds. Similarly, the molecular complex [Cr(HL^{2a})$_3$], **2a** also showed an intense transition at 560 nm, the intensity of which is much higher than that for the 565 nm transition in **3**. Moreover, the transition in **3** is sensitive to the nature of substitution (R) on the aryl ring of HL^2. For example, the transition in **3** shifts red from 555 to 580 nm on changing the para substitution from −Cl to −OCH_3. The frequencies of this transition (ν, cm^{-1}) for **3a**−**d** linearly correlate with Hammett's constant (σ).[15] We wish to note here that $E_{1/2}$ values for the Cr(III)/Cr(II) couple in the said complexes are less sensitive to the nature of substitution R (vide infra). Thus, the substitution on the aryl ring of HL^2 in **3** has a more pronounced effect on the visible range transition energies than on the metal redox potentials. These observations, in other words, suggest that the orbitals that are

---

(13) (a) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633. (b) Seal, A.; Ray, S. *Acta Crystallogr*. **1984**, *40C*, 929. (c) Majmudar, P.; Kamar, K. K.; Castiñeiras, A.; Goswami, S. *Chem. Commun*. **2001**, 1292.

(14) (a) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600. (b) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714. (c) Wolfgang, S.; Strekas, T. C.; Gafney, H. D.; Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2650.

(15) (a) Hammett, L. P. *Physical Organic Chemnistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Mukherjee, R. N.; Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 785.

Table 2. Optical Spectral Data

compd	absorption^a λ_{max}/nm (ϵ/M^{-1} cm^{-1})	IR(KBr) (υ, cm^{-1})		
		υ(C=N)	υ(N=N)	υ(ClO$_4$)
$[Cr(L^{1a})_2](ClO_4)$	1100^b (980), 850^b (5740), 750 (7900) 570^b (9220), 510 (13640), 360^b (17660)	1595	1305, 1250	1090, 620
$[Cr(L^{1a})_2]$	1460^b (950), 1250^b (945), 860^b (3000), 740^b (8080), 680^b (7690), 550 (12810), 480^b (9370), 340^b (16360)	1595	1310, 1265	
$[Cr(L^{1b})_2](ClO_4)$	1130^b (780), 880^b (2810), 750 (6720), 570^b (7810), 500 (11250), 360^b (16250)	1600	1300, 1240	1090, 615
$[Cr(L^{1b})_2]$	1460^b (1000), 1250^b (1020), 870^b (3180), 740^b (8550), 680^b (8100), 550 (13500), 480^b (10690), 340^b (18500)	1595	1310, 1265	
$[Cr(HL^{2a})_3]$	850^b (2630), 560 (38680), 330^b (27370)	1565	1355, 1315	
$[Cr(pap)_3]^c$	800^b (1320), 640^b (3680), 470 (13950), 330 (32110)	1600	1340	
$[CrCl_2(pap)(HL^{2a})]$	1415 (5315), 750^b (2635), 565 (20800), 335^b (17325), 275^b (19930)	1585	1305, 1220	
$[CrCl_2(pap)(HL^{2a})]^{+,d}$	1010 (2470), 670^b, 605 (24330), 420^b, 340^b			
$[CrCl_2(pap)(HL^{2a})]^{-,e}$	970 (1480), 765^b, 665^b, 605^b, 535^b, 465 (13830), 380^b, 350 (20870), 305^b			
$[CrCl_2(pap)(HL^{2b})]$	1415 (2485), 745^b (2965), 575 (29900), 340^b (26640), 265^b (31970)	1590	1305, 1220	
$[CrCl_2(pap)(HL^{2c})]$	1400 (3105), 755^b (4000), 580 (36370), 300^b (37155), 255^b (46480)	1595	1295, 1220	
$[CrCl_2(pap)(HL^{2d})]$	1425 (4370), 745^b (2295), 555 (30290), 285^b (39150), 245^b (47535)	1580	1300, 1215	

^{a} Solvent CH_3CN. ^{b} Shoulder. ^{c} Reference 10. ^{d} Generated by electrolysis at 0.50 V. ^{e} Generated by electrolysis at −0.50 V.

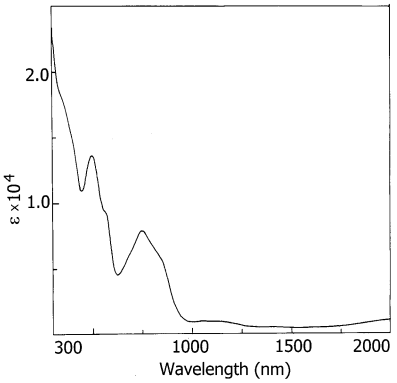


Figure 3. Solution electronic spectrum of $[Cr(L^{1a})_2](ClO_4)$.

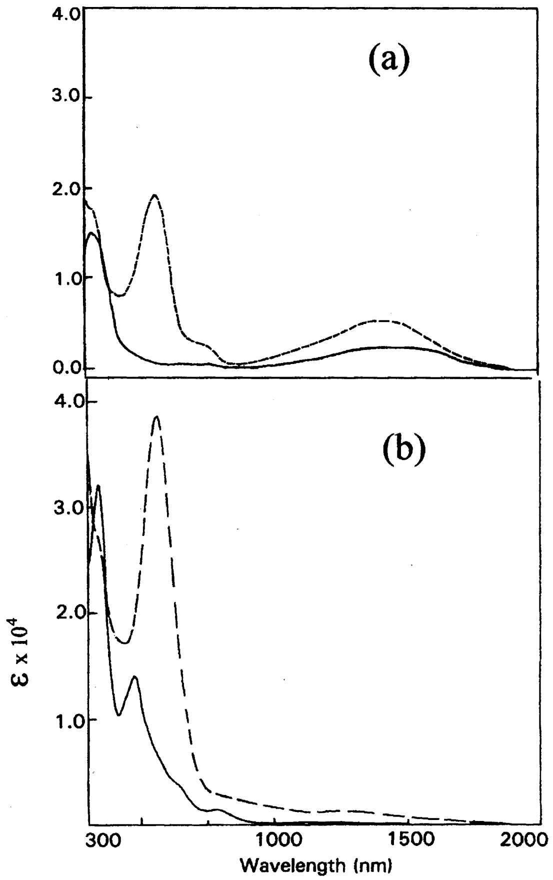


Figure 4. Solution spectra of (a) $[CrCl_2(pap)_2]$ (−), $[CrCl_2(pap)(HL^{2a})]$ (···) and (b) $[Cr(pap)_3]$ (−), $[Cr(HL^{2a})_3]$ (···).

involved in the above transition in the chromium complexes **3a**−**d** are predominantly ligand in character [N(amine) → (azo) transition]. Furthermore, the transition, under consideration, is appreciably solvatochromic. The solution colors of **3** in hydroxilic solvents are blue while those in other solvents are blue-violet. Complex **3** also showed a far red band near 1415 nm, which is assigned[9] to the ligand-to-metal (LMCT) charge-transfer transition.

Redox Behavior. The electrochemical behavior of the chromium complexes was probed in acetonitrile solution by cyclic volammetry. Voltammetric data are collected in Table 3 and representative volammograms are displayed in Figures 5 and 6.

(a) $[Cr^{III}(L^1)_2](ClO_4)$, [1](ClO$_4$): The chromium(III) complexes of the anionic ligand $[L^1]^-$, $[Cr(L^1)_2](ClO_4)$, showed two anodic and two cathodic responses. The lowest potential cathodic response is reversible and occurs near 0.0 V. This has been assigned to the Cr(III)/Cr(II) couple. The anodic wave at 1.0 V is electrochemically reversible, which follows another irreversible anodic wave at ca. 1.7 V. These two anodic responses are attributed[4,5] to ligand oxidations. The redox process near −1.0 V showed a much larger current height as compared to other one-electron-transfer processes. This is attributed[4] to reduction of the coordinated ligands. A few ill-defined cathodic responses with small current height appeared when the cathodic scan was allowed beyond −1.2 V. These are due to electrogenerated species that are formed following the ligand reductions. Similar multiple electron-transfer processes were also observed[3,4] in the other complexes of the anionic ligand $[L^1]^-$. Notably the observed potentials for [**1b**]$^+$ are cathodic by ca. 100 mV compared to those of [**1a**]$^+$, which is attributed to the effect of the electron-donating methyl substituent in the ligand. Such low potentials for the Cr(III)/Cr(II) couple in [**1**]$^+$ persuaded us to try and isolate the corresponding chromus complex, **1**, in the pure state. Fortunately, with hydrazine as the reducing agent, we were able to isolate a representative chromium-

Table 3. Cyclic Voltammetric Data[a]

compd	oxidation $E_{1/2}$(V)	reduction $E_{1/2}$(V)
$[Cr(L^{1a})_2](ClO_4)$	0.96, 1.69[b]	0.05, −1.19
$[Cr(L^{1b})_2](ClO_4)$	0.70, 1.29[b]	−0.19, −1.08[c]
$[Cr(HL^{2a})_3]$	0.31, 0.70	−0.31, −1.11, −1.42[d]
$[CrCl_2(pap)(HL^{2a})]$	0.37, 1.33[b]	−0.35, −1.12[d]
$[CrCl_2(pap)(HL^{2b})]$	0.36, 1.25[b]	−0.37, −1.14[d]
$[CrCl_2(pap)(HL^{2c})]$	0.34, 1.10[b]	−0.38, −1.10[d]
$[CrCl_2(pap)(HL^{2d})]$	0.37, 1.40[b]	−0.33, −1.15[d]
$[Cr(pap)_3]$[e]	0.50, 1.05	−0.20, −1.10, −1.48, −1.70[d]

[a] Experiments were carried out in CH_3CN at 298 K with TEAP as supporting electrolyte. The reported data correspond to a scan rate of 50 mV s^{-1}. [b] Irreversible anodic response; the potential corresponds to E_{pa}. [c] Quasireversible cathodic response; the potential corresponds to E_{pc}. [d] Irreversible cathodic response; the potential corresponds to E_{pc}. [e] Reference 10.

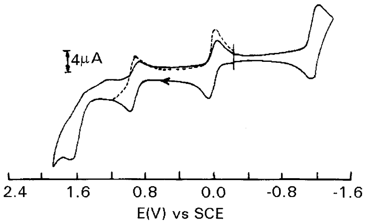


Figure 5. Segmented cyclic voltammogram of $[Cr(L^{1a})_2](ClO_4)$.

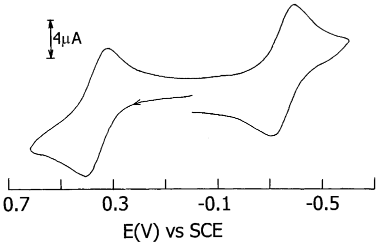


Figure 6. Segmented cyclic voltammogram of $[CrCl_2(pap)(HL^{2a})]$.

(II) complex, **1a** (violet), in almost quantitative yield. The compound is thermally stable but air sensitive, and is slowly reoxidized to [**1a**]$^+$ on prolong exposure to air. In solution, complex **1a** is a nonelectrolyte. It showed multiple charge transfer in the visible region (Table 2). Under identical conditions, the voltammogram of **1a** (initial scan anodic) is superposable on that of the corresponding [**1a**]$^+$ (initial scan cathodic) showing that the redox process, $[Cr(L^1)_2]^+ \rightleftharpoons [Cr(L^1)_2]$, is chemically reversible. Upon exhaustive constant potential oxidation of the complex, **1a** at +0.25 V, the coulomb count corresponds to one electron, the oxidized solution is brown, and its absorption spectrum matches quantitatively with that of [**1a**]$^+$.

(b) $[Cr(HL^2)_3]$, 2: The trischelate $[Cr(HL^2)_3]$, **2** displayed multiple CV responses in the potential range +1.5 to −1.5 V. Two of these are reversible anodic. There are three cathodic responses, of which the response at the lowest potential was irreversible. The cathodic responses are assigned to ligand reductions. The LUMO of the ligand, HL^2, like the parent pap ligand, can accommodate[6] up to two electrons. Therefore, successive six-electron reductions in the tris-chelate may be expected in $[Cr(HL^2)_3]$. However, three successive one-electron-transfer processes were observed in our experimental conditions. Notably, the ligand reductions in the tris-chelate **2** were systematically cathodic[10] as compared to those in $[Cr(pap)_3]$. This may be attributed to the strong inductive effect of *p*-NH(Ar) substitution in **2**. Similarly, the anodic response in **2** is more cathodic than the corresponding two anodic responses in $[Cr(pap)_3]$. The $E_{1/2}$ values of the $[Cr(HL^2)_3]$ and $[Cr(pap)_3]$ complexes are collected in Table 3 for comparison.

(c) $[CrCl_2(pap)(HL^2)]$, 3: Successive electron-transfer processes are the main features for the chromium dihalo complxes $[CrCl_2(pap)(HL^2)]$, **3**. Two reversible responses, one anodic (ca. 0.35 V) and another cathodic (ca. −0.35 V), are assigned[11] due to Cr(II)/Cr(III) and Cr(II)/Cr(I) couples, respectively. The responses for the corresponding couples[9] in the parent complex, $[CrCl_2(pap)_2]$, appeared at ca. 0.42 and ca. −0.30 V, respectively. Cathodic shift of these potentials in moving from $[CrCl_2(pap)_2]$ to $[CrCl_2(pap)(HL^2)]$ is primarily due to the inductive effect of the *p*-NH(Ar) group in HL^2. However, the effect of substitution on the ligand HL^2 has only an insignificant effect on the potentials of these responses. In addition, an anodic (irreversible) wave at >1.30 V was also observable in **3**, which, by contrast, is absent in the $[CrCl_2(pap)_2]$. This anodic wave in **3** may thus be assigned to ligand oxidation. An ill-defined ligand reduction wave was observed in **3** at potentials > −1.0 V. It may be noted here that electrochemical reductions[16] of metal dihalo complexes of 2-(arylazo)pyridine are generally ill-behaved due to halide dissociation.

To gain further insight into the nature of the strong visible range transition in **3,** we examined the complex **3a** spectroelectrochemically in acetonitrile. As the compound was oxidized at +0.50 V, the low-energy IR band (1415 nm) disappeared and a new broad band with much diminished intensity appeared at 1010 nm. Interestingly the strongest visible range transition at 565 nm in the original complex **3a** is red shifted to 605 nm in [**3a**]$^+$ and increased intensity consistent with its assignment as an intraligand charge-transfer process. The visible range transitions in the reduced complex [**3a**]$^-$, which were associated with three shoulders at 535, 605 and 665 nm, shifted blue (465 nm) and with much reduced intensity.

Conclusion

Two interesting classes of new chromium complexes with two positional isomers of 2-[(*N*-arylamino)phenylazo]pyridine have been synthesized successfully. The presence of the combination of hard and soft binding sites in the deprotonated $[L^1]^-$ makes them excellent ligands for stabilizing the metal ion in two different oxidation states. The coordination mode of the other isomer HL^2 is totally different. This acts as a neutral, strong π-acceptor bidentate ligand. Interestingly, the ligand HL^2 bears an uncoordinated donor amine function, which is separated from a coordinated acceptor azo function by a conjugated spacer. Strong intraligand charge-transfer transitions in the complexes of HL^2 are noted. Our work on the exploration of the coordination chemistry of HL^2 is in progress. Indications are strong

---

(16) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246.

that some of these might turn out to be complexes with nonlinear optical properties.

Experimental Section

The starting complexes[9,11] $[CrCl_2(pap)_2]$, $[Cr(pap)_3]$, and $[Cr(pap)_3](ClO_4)$ and the ligands[3,4] HL^1 and HL^2 were prepared by the reported method. Solvents and chemicals used for synthesis were of analytical grade. The supporting electrolyte tetraethylammonium perchlorate and solvents for electrochemical work were obtained as before.[5] Perchlorate salts of metal complexes are generally explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

Physical Measurements. A JASCO V-570 spectrometer was used to record electronic spectra. The IR spectra were obtained with a Perkin-Elmer 783 spectrophotometer. ^1H NMR spectra in $CDCl_3$ were recorded on a Bruker Avance DPX 300 spctrophotometer with $SiMe_4$ as internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C,H,N). Electrochemical measurements performed under a dry nitrogen atmosphere on a PAR model 370-4 electrochemistry system in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium-ferrocene couple under our conditions is 0.40 V. Magnetic moment measurements were carried out with a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrical conductivity was measured by using a Systronics Direct Reading Conductivity meter 304.

$[Cr(L^{1a})_2](ClO_4)$, [1a](ClO_4): The ligand HL^{1a} (0.1 g, 0.36 mmol) was dissolved in 25 mL of absolute ethanol and 1−2 drops of trimethylamine was added. To this deprotonated ligand solution was added a methanolic solution of $CrCl_3{\cdot}6H_2O$ (0.05, 0.18 mmol) and the mixture was refluxed in a water bath for 2 h. The color of the solution changed from orange yellow to reddish brown. The crude product was then purified by preparative TLC. The major reddish-brown part was separated with use of 4:1 $CHCl_3-CH_3CN$ as the eluant. The reddish-brown band was collected and 5 mL of a dilute aqueous solution of $NaClO_4$ was added to it. The dark brown compound thus obtained was recrystallized from a dichloromethane−hexane solvent mixture. Yield: 50%. Anal. Calcd for $C_{34}H_{26}N_8ClO_4Cr$: C, 58.49; H, 3.73; N, 16.06. Found: C, 59.02; H, 4.31; N, 16.43. Λ_m: 140 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M in CH_3CN). μ_{eff}(300 K): 3.80 μ_B. Similarly, $CrCl_3{\cdot}6H_2O$ was reacted with HL^{1b} in a 1:2 ratio in methanolic solution in the presence of 1−2 drops of trimethylamine as a base to produce the complex $[Cr(L^{1b})_2](ClO_4)$, [**1b**](ClO_4). Yield: 45%. Anal. Calcd for $C_{36}H_{30}N_8ClO_4Cr$: C, 59.55; H, 4.14; N, 15.44. Found: C, 59.87; H, 4.43; N, 16.06. Λ_m: 135 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M in CH_3CN). μ_{eff}(300 K): 3.75 μ_B.

$[Cr(HL^{2a})_3]$, 2a: The ligand HL^1 (0.1 g, 0.36 mmol) and $Cr(CO)_6$ (0.027 g, 0.12 mmol) were added to 15 mL of *n*-octane. It was refluxed for 6 h. A dark compound was precipitated and the color of the solution became yellowish-blue. The mixture was cooled and the precipitate was collected by filtration. It was then recrystallized from a dichloromathane−hexane solvent mixture. Yield: 30%. Anal. Calcd for $C_{51}H_{42}N_{12}Cr$: C, 70.02; H, 4.46; N, 19.22. Found: C, 69.76; H, 4.90; N, 19.45. μ_{eff}(300 K): diamagnetic.

Table 4. Crystallographic Data of the Compounds [**1a**](ClO_4) and **3a**

	[**1a**](ClO_4)	**3a**
empirical formula	$C_{34}H_{26}ClCrN_8O_4$	$C_{28}H_{23}Cl_2CrN_7$
molecular mass	698.08	580.43
temp [K]	293(2)	213(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a [Å]	9.1815(12)	28.666(2)
b [Å]	10.3470(14)	11.8843(3)
c [Å]	17.220(2)	17.5429(10)
α [deg]	103.975(3)	90
β [deg]	91.119(3)	107.729(4)
γ [deg]	93.829(3)	90
V [Å^3]	1582.9(4)	5692.6(5)
Z	2	8
$D_{calc.}$ [Mg/m^3]	1.465	1.355
cryst dimen [mm^3]	0.56 × 0.13 × 0.07	0.20 × 0.15 × 0.10
θ range for data collection [deg]	1.22−27.54	5.11−64.98
GOF	1.022	0.957
wavelengths [Å]	0.71073	1.54184
reflns collected	10266	5716
unique reflns	7069	4700
largest diff between peak and hole [e Å^{-3}]	0.599, −0.462	0.366, −0.509
final R indices [$I > 2\sigma(I)$]	R1 = 0.0569 wR2 = 0.1002	R1 = 0.0610 wR2 = 0.1415

$[CrCl_2(pap)(HL^{2a})]$, 3a: A mixture of $[CrCl_2(pap)_2]$ (0.1 g, 0.204 mmol) and aniline (0.5 mL) was heated neat on a steam bath for 4 h. The cooled mixture was thoroughly washed with diethyl ether. The blue-violet crude product was then purified on a preparative silica gel TLC plate and a violet band was eluted with chloroform as the eluant. Finally it was crystallized from a dichloromethane−hexane solvent mixture. Yield: 30%. Anal. Calcd for $C_{28}H_{23}N_7Cl_2Cr$: C, 57.93; H, 3.97; N, 16.89. Found: C, 57.10; H, 4.15; N, 16.35. μ_{eff}(300 K): 2.83 μ_B. The other chromium complexes were synthesized similarly. Their yields and analytical data are collected below.

$[CrCl_2(pap)(HL^{2b})]$, 3b: Yield: 35%. Anal. Calcd for $C_{29}H_{25}N_7Cl_2Cr$: C, 58.58; H, 4.21; N, 16.50. Found: C, 58.84; H, 4.45; N, 16.77. μ_{eff}(300 K): 2.77 μ_B.

$[CrCl_2(pap)(HL^{2c})]$, 3c: Yield: 30%. Anal. Calcd for $C_{29}H_{25}N_7Cl_2OCr$: C, 57.05; H, 4.10; N, 16.07. Found: C, 58.40; H, 4.81; N, 16.45. μ_{eff}(300 K): 2.72 μ_B.

$[CrCl_2(pap)\ (HL^{2d})]$, 3d: Yield: 35%. Anal. Calcd for $C_{28}H_{22}N_7Cl_3Cr$: C, 54.68; H, 3.58; N, 15.94. Found: C, 55.14; H, 3.51; N, 15.14. μ_{eff}(300 K): 2.86 μ_B.

Chemical reduction of $[1]^+ \rightarrow [1]$. A 25-mL dichloromethane solution of [**1a**](ClO_4) (0.10 g, 1.43 mmol) was stirred with 5 mL of dilute aqueous hydrazine solution at room temperature for 30 min. The color of the solution changed from reddish brown to violet. The above mixture was extracted with dichloromethane (2 × 10 mL), which was then dried with anhydrous sodium sulfate. The dried solution was concentrated to half of the initial volume. Slow addition of hexane to the above violet solution precipitated dark microcrystals of **1a**. This was further crystallized from a dichloromethane−hexane solvent mixture. Yield: 95%. Anal. Calcd for $C_{34}H_{26}N_8Cr$: C, 68.23; H, 4.35; N, 18.73. Found: C, 68.44; H, 4.52; N, 18.87. Similarly, [**1b**](ClO_4) was treated with dilute hydrazine in dichloromethane at room temperature to produce crystalline $[Cr(L^{1b})_2]$, **1b**. Yield: 90%. Anal. Calcd for $C_{36}H_{30}N_8Cr$: C, 69.00; H, 4.79; N, 17.89. Found: C, 68.87; H, 4.59; N, 18.02.

X-ray Structure Determination. The crystal data of [**1a**](ClO_4) and **3a** are collected in Table 4.

$[Cr(L^{1a})_2](ClO_4)$, [1a](ClO_4): X-ray quality crystals (0.56 × 0.13 × 0.07 mm^3) of [**1a**](ClO_4) were obtained by slow diffusion of a dichlromethane solution of the complex into hexane. The data were collected on a Bruker SMART diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz−polarization effects. A total of 10266 reflections were collected, of which 7069 were unique (R_{int} = 0.0341). The structure was solved by employing the SHELXS 97 program package[17] and refined by full-matrix least squares based on F^2 (SHEXL 97).[18]

[CrCl$_2$(pap)(HL^{2a})], 3a: X-ray quality crystals (0.20 × 0.15 × 0.10 mm^3) of **3a** were obtained by slow diffusion of a dichloromethane solution of the complex into hexane. Cell parameters were obtained by least-squares fits of 25 machine-centered reflections. Data were collected (30.537° < θ < 49.801°) on a Enraf Nonius CAD4 automatic diffractometer[19] (213 K), using Cu Kα radiation (λ = 1.54184 Å). Data were corrected for Lorentz−polarization effects.[20] Of the 5716 reflections collected, 4700 were unique (R_{int} = 0.0598) and 4700 reflections satisfying [$I > 2\sigma(I)$] were used for structure solution by direct methods[17] and refined by a full-matrix least-squares procedure with use of anisotropic displacement parameters[18] on F^2, using SHELXL 97. All the hydrogen atoms were located in their calculated positions (CH 0.93−0.97 Å) and were refined with use of a riding model.

Acknowledgment. We thank the Council of Scientific and Industrial Research and the Department of Science and Technology, New Delhi for financial support. The authors are indebted to Professor M. D. Ward and Dr. R. L. Paul for the spectroelectrochemical measurements on one of the compounds.

Supporting Information Available: X-ray crystallographic details, in CIF format, of two compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0201497

---

(17) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *46A*, 467.

(18) Sheldrick, G. M. *SHELXL 97*, Program for the refinement of crystal structures; University of Goettingen: Goettingen, Germany, 1997.

(19) Nonius, B. V. *CAD 4−Express Software*, Ver. 5.1/1.2 Enraf Nonius; Delft, The Netherlands, 1994.

(20) Kretschmar, M. *GENHKL*, Program for the reduction of CAD 4 Diffreactometer data; University of Tuebingen: Tuebingen, Germany, 1997.