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Synthesis, characterization and toxicity of new heterobimetallic complexes of platinum(II) and palladium(II)

Kripa Sharma, Nighat Fahmi and R.V. Singh*
Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Heterobimetallic complexes of the type $[M(C_6H_6N_2)_2(M')_2(R)_4]Cl_2$ have been synthesized by the direct reaction of $[M(C_6H_8N_2)_2]Cl_2$ with Group 4 or 14 organometallic dichlorides $Ph_2M'Cl_2$, $Me_2M'Cl_2$ or $Cp_2M''Cl_2$ in 1:2 molar ratio in MeOH (M = Pd or Pt, M′ = Si or Sn and M″ = Ti or Zr). The compounds were characterized by elemental analysis, molecular weight determination, electronic, ^{1}H NMR and IR spectra, magnetic susceptibilities and conductivity measurements. These studies showed that the compounds are monomers and dimagnetic in nature, with a square-planar geometry around palladium and platinum metals. Both the free ligands and their metal complexes were screened for antimicrobial activity on different species of pathogenic fungi and bacteria and were found active in this respect. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

The chemistry of macrocyclic hosts has experienced much growth in recent years. Final design of the macrocyclic compounds depends upon the stereochemical requirements and coordinating features of the metal ion.[1] Macrocyclic complexes are very active in metalloenzymes and industrial catalysis. Synthetic macrocyclic ligands resemble natural macrocycles, such as porphyrins, in electronic properties and reactivity. A large number of synthetic macrocyclic complexes have been obtained by the condensation of di- or poly-amines with aldehydes or ketones.[2] The macrocyclic ligands display a number of features of chemical interest.[3] These include the formation of both mononuclear and binuclear metal complexes. Many such complexes have unusual structures. Small substrate molecules and ions may be bound as bridging ligands between the metal centres in the dinuclear complexes.[4] These dinuclear complexes may be used as oxidation catalysts for organic substrates.[5]

Tetra-aza macrocycles have attracted considerable interest among inorganic chemists in recent years. An intriguing feature of these systems is that the size of the ligands can be changed with relative ease by synthetic means. By doing so, the enclosed metal ion behaves in different ways.[6] Diamine complexes of palladium(II) exhibit markedly greater kinetic and thermodynamic stability than the copper(II) and nickel(II) systems and offer a potential starting point for condensation reactions.[7] 1,2-Phenylene diamine may be used for the preparation of bimetallic complexes, and it shows typical electrophilic substitution reactions, such as acylation,[8] due to the electronic abundance in the phenyl rings. However, examples of heterobimetallic complexes of platinum(II) and palladium(II) with 1,2-phenylene diamine are limited. Therefore, we report the synthesis and spectroscopic characterization of such new heterobimetallic complexes of these metals.

EXPERIMENTAL

All the chemicals used for the synthesis of heterobimetallic complexes were of AR grade. The solvents MeOH and DMSO were distilled and dried before use.

* Correspondence to: R. V. Singh, Department of Chemistry, University of Rajasthan, Jaipur 302004, India.
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Table 1 Physical properties and analytical data of ligands and their complexes

Complex	Colour	M.p. (°C)	Analysis (%)[a]				Mol. Wt.[a]
			M	M′ or M″[b]	N	Cl	
$[Pd(C_6H_8N_2)_2]Cl_2$	Dark brown	246	26.99 (27.03)	—	14.19 (14.23)	17.18 (18.01)	369.58 (393.58)
$[Pd(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	Purple	209	10.98 (11.37)	25.34 (25.37)	5.96 (5.99)	7.35 (7.58)	926.59 (935.33)
$[Pd(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	Reddish brown	140	15.21 (15.48)	34.52 (34.55)	7.96 (8.15)	10.29 (10.31)	669.21 (687.06)
$[Pd(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	Brown	161	13.98 (14.11)	7.42 (7.45)	7.26 (7.42)	9.27 (9.40)	729.00 (754.11)
$[Pd(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	Dark brown	280(d)	13.87 (14.27)	12.82 (12.85)	7.28 (7.51)	9.46 (9.50)	722.68 (745.68)
$[Pd(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	Red	205	12.75 (12.78)	21.89 (21.91)	6.42 (6.73)	8.47 (8.51)	809.23 (832.35)
$[Pt(C_6H_8N_2)_2]Cl_2$	Black	>300	41.41 (40.45)	—	11.42 (11.61)	14.68 (14.70)	459.29 (482.24)
$[Pt(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	Dark brown	240	19.02 (19.05)	23.00 (23.18)	5.42 (5.47)	6.88 (6.92)	996.99 (1023.99)
$[Pt(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	Brown	>300	27.52 (27.56)	33.25 (33.54)	7.64 (7.91)	9.98 (10.01)	685.70 (707.7)
$[Pt(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	Dark brown	169	22.88 (23.14)	6.62 (6.66)	6.37 (6.64)	8.39 (8.41)	822.74 (842.77)
$[Pt(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	Reddish brown	202(d)	23.34 (23.38)	11.43 (11.47)	6.43 (6.71)	8.46 (8.49)	831.25 (834.33)
$[Pt(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	Red	>300	20.96 (21.18)	19.67 (19.80)	6.05 (6.08)	7.66 (7.69)	890.01 (921.01)

[a] Found (calc.).
[b] Percentage of M′ or M″.

Synthesis of $[M(C_6H_8N_2)_2]Cl_2$

The synthesis of $[M(C_6H_8N_2)_2]Cl_2$ was carried out by dissolving MCl_2 (0.01 mol) in hot MeOH in a 100 ml R.B. flask. The requisite amount of 1,2-phenylene diamine was added in 1:2 stoichiometric proportions. The solution mixture was stirred for 12–14 h. The product was washed and recystallized from methanol and dried under vacuum. The reaction proceeded as shown in (Eqn [1]).

$$MCl_2 + 2C_6H_8N_2 \rightarrow [M(C_6H_8N_2)_2]Cl_2 \quad [1]$$

Synthesis of heterobimetallic complexes

$[M(C_6H_8N_2)_2]Cl_2$ (0.01 mol) was treated with Group 4 or 14 organometallic dichlorides, $Ph_2M'Cl_2$, $Me_2M'Cl_2$ and $Cp_2M''Cl_2$ (0.02 mol) in hot MeOH. In each reaction, solid products were obtained after keeping the reaction mixture overnight at room temperature. The products formed were washed with hot MeOH and dried under vacuum. Their physical properties and analytical data are given in Table 1.

Analytical methods and physical measurements

Molar conductances of compounds were measured in 10^{-3} M DMF solution on a Systronic model 305 conductivity bridge. Molecular weights were determined by the Rast Camphor method. IR spectra were recorded on a Nicolet Megna FT-IR 550 spectrophotometer in KBr pellets. ^{1}H NMR spectra were recorded on a JEOL FX-90Q spectrometer in DMSO-d_6 using TMS as the internal standard. Electronic spectra were recorded on a Varian Cary/2390 spectrophotometer and magnetic measurements on a Model 155 vibrating sample magnetometer at the RSIC, IIT Madras. Palladium, was estimated gravimetrically.[9] Platinum, titanium, zirconium, tin and silicon were estimated gravimetrically as their oxides.[9] Nitrogen was estimated by Kjeldahl's method and chlorine by Volhard's method.

Microbial activity

The growing interest in biochemical applications and an interest in better fungicides and bactericides have prompted us to screen all the newly synthesized heterobimetallic derivatives with their ligands.

Antifungal activity

The fungi were grown in agar medium prepared by dissolving glucose (20 g), starch (20 g), agar–agar (20 g) and 1000 ml of distilled water at 25 ± 2 °C. Compounds with 125 and 250 ppm concentrations in MeOH were mixed in the medium using a small amount of DMF for initial solution. The linear growth of the fungus was obtained by measuring the diameter of the colony on Petri plates after 4 days (96 h), and the percentage inhibition was calculated by the relationship $(C - T)100C^{-1}$; C and T are the diameters of the fungal colony in the control and test plates respectively. Fungi were grown on PDA slants. After 7 days of growth, 5 ml of sterilized distilled water was added to the test tube, which was shaken vigorously. 0.5 ml of the resulting spore suspension of fungi was placed on to PDA plates. The concentrations of fungicides tested were 0.250 mg ml^{-1} (250 ppm) and 0.125 mg ml^{-1} (125 ppm).

Antibacterial activity

The bactericidal activity was evaluated by the paper disc plate method. A nutrient agar medium [peptone (5 g), beef extract (5 g), NaCl (5 g) and agar-agar (20 g) in 1000 ml of distilled water] and 5 mm diameter discs of Whatman No. 1 paper were used. The compounds were dissolved in a small amount of DMF and made up by dry MeOH to 500 and 1000 ppm concentrations. The filter paper discs were soaked in the different solutions of the compounds, dried and then placed on the Petri plates previously seeded with the test organisms. The plates were incubated for 36 h at 30 ± 1 °C and the inhibition around each disc was measured. One loop full of bacteria was taken into a test tube containing 5 ml of sterilized distilled water and shaken vigorously to dislodge bacterial cells. After that, 0.5 ml of bacteria suspension was poured over the nutrient agar plate. Bactericidal concentrations tested were 1 mg ml^{-1} (1000 ppm) and 0.5 mg ml^{-1} (500 ppm).

Mode of action

The compounds inhibit the growth of fungi and bacteria to a greater extent as the concentration increased. The mechanism of toxicity may be due to the inhibition of energy production or ATP production,[10] for instance by inhibition of respiration or by uncoupling of oxidative phosphorylation. The energy-producing processes are located partly

Table 2 Fungicidal screening data of ligands and their heterobimetallic complexes

	Average inhibition after 96 h (%)			
	Alternaria alternata		*Fusarium oxysporum*	
Compound	125 ppm	250 ppm	125 ppm	250 ppm
$[Pd(C_6H_8N_2)_2]Cl_2$	25	33	27	35
$[Pd(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	38	44	41	55
$[Pd(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	45	55	49	61
$[Pd(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	50	66	55	78
$[Pd(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	28	37	31	38
$[Pd(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	32	40	38	43
$[Pt(C_6H_8N_2)_2]Cl_2$	22	31	23	30
$[Pt(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	34	40	37	50
$[Pt(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	41	52	46	59
$[Pt(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	49	63	54	74
$[Pt(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	26	34	25	33
$[Pt(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	31	39	35	47

* Results as percentages.

in the cytoplasm and partly in the mitochondria. Inhibition of such processes will eventually have a fungicidal and bacterial effect.

On the basis of the above studies, it may be concluded that fungitoxicity and bacteriotoxicity of a compound may be significantly enhanced on chelation with the metal ion. Data for fungicidal and bacterial activities are recorded in Tables 2 and 3.

RESULTS AND DISCUSSION

Elemental analysis and spectral studies showed the formation of $[M(C_6H_8N_2)_2]Cl_2$ as well as the bimetallic complexes[11–13] $[M(C_6H_6N_2)_2(M')_2(R)_4]Cl_2$. The reactions proceeded as shown in Eqn [2].

$$[M(C_6H_8N_2)_2]Cl_2 + 2R_2M'Cl_2 \xrightarrow{MeOH} [M(C_6H_6N_2)_2(M')_2(R)_4]Cl_2 \quad [2]$$

where, M = Pt and Pd; M′ = Si and Sn and R = Ph and Me.

Similar reactions were also carried out with $Cp_2M''Cl_2$ (M″ = Ti and Zr). All the complexes are stable at room temperature and are non-hygroscopic in nature. The resulting coloured solids are sparingly soluble in cold organic solvents, such as MeOH, EtOH, CCl_4, and benzene, but are completely soluble in hot solvents, as well as in cold DMF and DMSO. Molecular weight determinations showed that they are monomeric in nature. They are diamagnetic, as indicated by magnetic measurements. The high values of the molar conductivities (180–260 $\Omega^{-1}\,mol^{-1}\,cm^2$) of the complexes in anhydrous DMF showed that they behave as 1:2 electrolytes.

IR spectra

The IR spectra of the ligands and their complexes were recorded and a comparative study confirmed the formation of heterobimetallic complexes with the proposed coordination pattern. The primary amine exhibits a band at higher frequency than that of the corresponding secondary amine. A strong band appeared in the range 3214–3252 cm^{-1} and was assigned to ν(N—H) in the case of $[Pd(C_6H_8N_2)_2]Cl_2$ and $[Pt(C_6H_8N_2)_2]Cl_2$; and this shifted to the lower frequency side in the bimetallic complexes, indicating the formation of a Group 14 metal–nitrogen coordination bond.[14] Aromatic ring stretches (C—C)[15] appeared at 1643, 1528 and 1451 cm^{-1} and aromatic C—H and C—N stretches were assigned at 3057 cm^{-1} and 843 cm^{-1} respectively. IR bands occurring at ~3000 for ν(C—H), ~1430 for ν(C—C), ~1020 for δ(C—H) and ~810 cm^{-1} for δ(C—H) in the relevant complexes indicate the presence of the cyclopentadienyl ring.[16,17] The appearance of these cyclopentadienyl ring bonds indicates that this group remains as such in the complexes.

Two new weak bands also appear in the lower intensity region at 586 cm^{-1} and 420 cm^{-1} of the

Table 3 Antibacterial Activity of Ligands and their Complexes

	Diameter of inhibition zone after 36 h (mm)			
	Escherichia coli (−)		*Staphylococcus aureus* (+)	
Compound	500 ppm	1000 ppm	500 ppm	1000 ppm
$[Pd(C_6H_8N_2)_2]Cl_2$	3	5	2	3
$[Pd(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	4	6	3	4
$[Pd(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	5	8	4	6
$[Pd(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	6	10	7	5
$[Pd(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	4	5	2	3
$[Pd(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	4	6	3	4
$[Pt(C_6H_8N_2)_2]Cl_2$	2	3	2	2
$[Pt(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	3	4	3	3
$[Pt(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	6	7	4	6
$[Pt(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	5	7	6	9
$[Pt(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	2	5	3	3
$[Pt(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	2	4	3	4

* Results in mm.

relevant complexes. These bands are attributed to ν(Si⟶N)[18] and ν(Sn⟶N) vibrations respectively.

^{1}H NMR spectra

The proposed coordination pattern was evidenced by ^{1}H NMR spectra of the ligands, as well as of their corresponding bimetallic complexes in DMSO-d_6. The spectra of the ligands showed a signal due to primary amine protons. The disappearance of the amine proton signal and the appearance of a secondary amine proton signal around δ 8 ppm[11,19] in the spectra of complexes suggests the formation of the proposed macrocyclic framework. A singlet appearing in the spectra of complexes at δ 1.04–1.68 ppm is due to methyl protons. In addition, a singlet and a multiplet in the region δ 6.32–6.78 ppm and δ 7.01–7.96 ppm were observed in the spectra of complexes having cyclopentadienyl and phenyl rings respectively. It was also noted that amine and aromatic protons are observed in an average 1:2 integrated ratio. Chemical shift values relative to TMS are listed in Table 4.

Electronic spectra

The above conclusions are further supported by the electronic spectra of the ligands and their metal

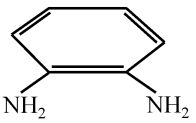
Table 4 ^{1}H NMR spectral data (δ, ppm) of ligands and their complexes[a]

Compound	−NH_2	−NH	Me and Cp	Ph
$[Pd(C_6H_8N_2)_2]Cl_2$	4.56	—	—	7.01–7.36
$[Pd(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	—	8.14	—	7.32–7.96
$[Pd(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	—	8.04	1.68	7.04–7.60
$[Pd(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	—	8.16	—	7.12–7.92
$[Pd(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	—	8.00	6.78	7.24–7.46
$[Pd(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	—	8.01	6.32	7.12–7.28
$[Pt(C_6H_8N_2)_2]Cl_2$	4.54	—	—	7.04–7.39
$[Pt(C_6H_6N_2)_2Sn_2(Ph)_4]Cl_2$	—	8.00	—	7.12–7.76
$[Pt(C_6H_6N_2)_2Sn_2(Me)_4]Cl_2$	—	8.03	1.04	7.26–7.30
$[Pt(C_6H_6N_2)_2Si_2(Ph)_4]Cl_2$	—	—	—	7.02–7.43
$[Pt(C_6H_6N_2)_2Ti_2(Cp)_4]Cl_2$	—	7.92	6.72	7.00–7.32
$[Pt(C_6H_6N_2)_2Zr_2(Cp)_4]Cl_2$	—	8.08	6.56	7.04–7.84

[a] Integrated areas show 1:2 ratios between RNH and aromatic protons.

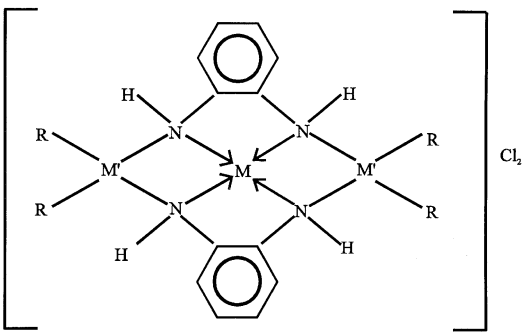
complexes. Palladium(II) and platinum(II) complexes display d–d spin-allowed transitions due to the three lower lying 'd' levels to the empty d_{x^2}–y^2 orbitals. Transitions are assigned from the ground state $^1A_{1g}$ to the excited states $^1A_2$, $^1B_{1g}$ and ^1E_g in order of increasing energy. Three d–d bands are observed in the range 519–525 nm, 455–480 nm and 440–451 nm in the present palladium complexes and 519–525 nm, 440–467 nm and 339–372 nm in the case of the platinum complexes. These bands are attributed to $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1E_g$ transitions respectively. These spectral values support a square-planar geometry around palladium(II) and platinum(II) ions and are in close agreement with those reported previously for square-planar complexes of these two metals.[20] Bands observed in the range 269–276 nm may be assigned to a π–π^* transition in the ligands. Further, bands appearing in the range 300–314 nm may be tentatively assigned to charge transfer in the complexes.[21]

$$MCl_2 + 2C_6H_8N_2 \xrightarrow[\text{Hot}]{\text{MeOH}} [M(C_6H_8N_2)_2]Cl_2$$



$$[M(C_6H_8N_2)_2]Cl_2 + 2R_2M'Cl_2 \xrightarrow[\text{Hot}]{\text{MeOH}}$$

R = Me, Ph and Cp



Scheme 1

CONCLUSIONS

The foregoing evidence supports the synthesis of heterobimetallic complexes. Scheme 1 may be proposed for the formation and structure of these complexes

Similar reactions were also carried out with $Cp_2M''Cl_2$. Related work has also been reported by other workers.[14,22] The microbial activity of the complexes and ligands showed that the tin compounds are more active than silicon. In the case of Ph_2SiCl_2 and Me_2SnCl_2, silicon compounds are more active than tin compounds due to the attachment of phenyl groups to the silicon atom.

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