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Heteroleptic Crown Thioether Chemistry. Synthesis and Characterization of the Group 9 Metal Complexes of 1,4,7-Trithiacyclononane

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Owing to the unique electronic and structural properties, 1,4,7-trithiacyclononane(9S3), a nine-membered crown thioether, has been successfully employed in the development of crown thioether chemistry.¹⁻³ Particularly, 9S3 derives its strong chelating ability from the retention of endodentate conformation on binding to a trigonal face of a metal, leading to an observation of large set of homoleptic complexes of lower oxidation state transition metal ions³ as well as *p*-block metal ion.⁴ On the other hand, heteroleptic 9S3 complexes, which appear in the form of metal carbonyls,⁵ metal halides,⁶ metal hydride,⁷ metal oxides⁸ or organometallic compounds,⁹ constitute a newly emerging class. Described herein are brief accounts of synthesis and structural characterization of the type [L_nM(9S3)]^{z+}, a set of novel heteroleptic crown thioether complexes with varying L, c and the Group 9 metal M.

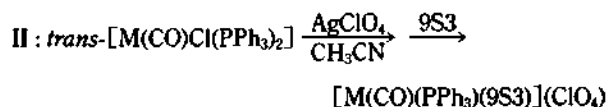
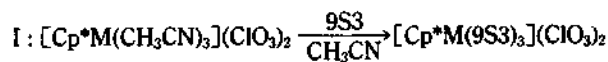
Dicationic [Cp^{*}M(9S3)]²⁺ (1: M=Co; 2: M=Rh; 3: M=Ir) and monocationic [M(CO)(PPh₃)(9S3)]⁺ (4: M=Rh; 5: M=Ir) were prepared as perchlorate salts according to the reaction Scheme I and II, respectively.¹⁰ In the Scheme I acetonitrile solutions of [Cp^{*}M(CH₃CN)₃](ClO₄)₂ (M=Co, deep purple;

Table 1. Spectroscopic Data for 9S3 Complexes of Group 9 Metals.

| [Cp [*] M(9S3)](ClO ₄) ₂ (CH ₃ CN) | | | |
|---|---|---|--|
| M | NMR | Cp [*] | 9S3 |
| Co | ¹ H (CD ₃ CN) ^a | 1.70 (s, 15H) | 2.91-3.16 (m, 12H) |
| | ¹³ C (CD ₃ CN) ^a | 10.2 (C ₅ Me ₅) 104 (C ₅ Me ₅) | 38.9 |
| | ¹ H (d ₆ -DMSO) | 1.94 (s, 15H) | 3.18-3.27 (m, 12H) |
| Rh | ¹³ C (d ₆ -DMSO) | 9.04 (C ₅ Me ₅) 106 (C ₅ Me ₅ , ¹ J _{Rh-C} =6.3 Hz) | 36.7 |
| | ¹ H (CD ₃ CN) | 2.04 (s, 15H) | 2.84-2.96 (m, 12H) |
| | ¹³ C (CD ₃ CN) | 9.27 (C ₅ Me ₅) 102 (C ₅ Me ₅) | 38.5 |
| [M(CO)(PPh ₃)(9S3)](ClO ₄) | | | |
| M | ν_{CO} ^b , cm ⁻¹ | ¹ H-NMR (d ₆ -DMSO) | ³¹ P{ ¹ H}-NMR ^c (d ₆ -DMSO) |
| Rh | 1950 | 2.41-2.73 (m, 12H, 9S3) 7.53-7.72 (m, 15H, PPh ₃) | 42.4 (d, <i>J</i> _{Rh-P} =128 Hz) |
| | | Ir | 1932 |

^a Referenced to TMS. ^b KBr. ^c Referenced to 85% aq H₃PO₄.

Rh, yellow; Ir, orange) were generated *in situ* by stirring the slurry of Cp^{*}Co(CO)I₂¹¹ or [Cp^{*}MCl₂]₂ (M=Rh, Ir) with stoichiometric amount of AgClO₄ in acetonitrile for 1.5-2 h followed by filtration. Addition of 9S3 to the filtrate, stirring the resulting solutions for a period of 12-18 h at r.t., and filtration resulted in orange-red, pale green and pale yellow solution for M=Co, Rh, and Ir, respectively. Recrystallization (CH₃CN/Et₂O) of the solids obtained by treating the foregoing solutions with large amount of Et₂O afforded analytically pure crystalline (ClO₄)₂ · 1 · (CH₃CN) (orange-red; 35%; Anal. Found (Calc.) C, 35.2 (35.2); H, 4.85 (4.92); N, 2.05 (2.28)), (ClO₄)₂ · 2 · (CH₃CN) (green; 80%; Anal. Found (Calc.): C, 32.3 (32.8); H, 4.59 (4.59); N, 1.85 (2.12)) and (ClO₄)₂ · 3 · (CH₃CN) (pale-yellow; 70%; Anal. Found (Calc.): C, 29.2 (28.9); H, 3.98 (4.04); N, 1.69 (1.87)). In the Scheme II, analogous work-up yielded spectroscopically pure



crystalline orange-red 4 · (ClO₄) and yellow 5 · (ClO₄).

Solid infrared spectra of [Cp^{*}M(9S3)](ClO₄)₂(CH₃CN) are all similar and contain the features of Cp^{*}, 9S3, ClO₄ and CH₃CN, which and other spectroscopic data listed in Table 1 indicate that the three complexes have the same structural core whose nature for M=Rh was determined by single crystal X-ray analysis.¹² The structure of cationic species 2, displayed in Figure 1, reveals endo-tridentate ligating nature

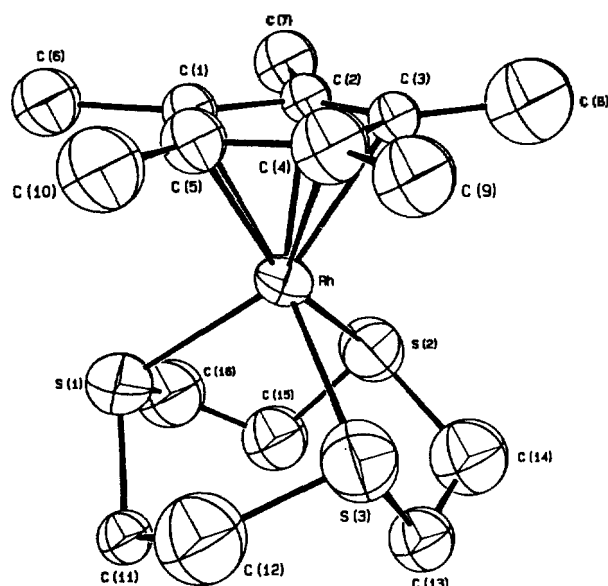


Figure 1. Structure of $[\text{Cp}^*\text{Rh}(9\text{S}3)]^{2+}$ (**2**) showing the atom labeling scheme. Selected average distances (\AA) and angle (deg) with standard deviation in parenthesis: Rh-S, 2.340(7); Rh-C (Cp* ring), 2.184(9); S-Rh-S, 88.3(7) $^\circ$.

of 9S3 to Rh with average Rh-S distance of 2.340(7) \AA and average S-Rh-S angle of 88.3(7) $^\circ$. The observed Rh-S distances in **2** are similar to those in $[\text{Rh}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)_3$ (average 2.341(6) \AA)¹³ and constitute rare¹⁴ example of Rh(III)-SR₂ (R = sp³-C) bonding interaction. The relative extent of trigonal flattening of 9S3, measured by chelating S-M-S angles, in **2** is similar to $[\text{Rh}(9\text{S}3)_2]^{3+}$ (average 88.6 $^\circ$),¹³ but lesser compared to $[\text{Cp}^*\text{Fe}(9\text{S}3)]^+$ (average 90.6 $^\circ$).^{9a}

Unlike the analogs of its heavier congener, the formation of **1** does not proceed when AgBF₄ or AgCF₃SO₃ is adopted instead of AgClO₄. In addition, the reaction system of Cp*Co(CO)I₂/9S3/NaBPh₄, which is under investigation, seems to lead to a new heteroleptic 9S3 complex involving three different ligands around Co(III). The class of heteroleptic 9S3 complexes with more than two different ligands is rare in example.^{9c} The IR and NMR spectroscopic data (Table 1) of ClO₄⁻ salt of **4** and **5** confirmed the foregoing class of heteroleptic 9S3 complexes of Rh(I) and Ir(I). The mononuclear cation **5** is also accessible¹⁵ via the reaction of $[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3\text{CN})](10\text{-endo-SnPh}_3\text{-nido-7,8-C}_2\text{B}_9\text{H}_{11})$ ¹⁶ with 9S3. Currently, synthesis of heteroleptic 9S3 complexes containing nido-7,8-C₂B₉H₁₁²⁻ as a coligand is in progress.

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10. The preparation of cation **2**, **3** and **4** has been claimed but no appropriate structural or spectroscopic data were reported. For **2** and **3**, see the following: M. N. Bell, A. J. Blake, M. Schröder, and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.*, 471 (1986); A. J. Blake and M. Schröder, In "Advances in Inorganic Chemistry", A. G. Sykes, Ed., Academic Press, Inc., New York, Vol. 35, p. 22 (1990). For **4**, see the reference 9c of this paper.
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12. Crystallographic data for $(\text{ClO}_4)_2 \cdot 2 \cdot (\text{CH}_3\text{CN})$: C₁₈H₃₀Cl₂NO₈RhS₃, Orthorhombic, *Pna*2₁, *a* = 31.548(5), *b* = 9.753(2), *c* = 8.629(2) \AA , *V* = 2654.9(8) \AA^3 , *Z* = 4, *D_c* = 1.651 gcm⁻³, 2 θ_{max} = 44 $^\circ$, *R* = 0.0816 for 1055 reflections (*I* > 3 σ (*I*)). Crystal data were collected on an Enraf-Nonius CAD 4 diffractometer at ambient temperature using Mo-K α radiation and corrected for Lorentz, polarization and absorption effects.
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15. Isolated as $[10\text{-endo-SnPh}_3\text{-}\mu\text{-H-7,8-nido-C}_2\text{B}_9\text{H}_{10}] \cdot 5$: IR (KBr), ν_{BH} = 2521, ν_{BHSn} = 2390, ν_{CS} = 825 cm⁻¹; ¹¹B{¹H}-

NMR ($\text{CH}_3\text{CN}/10\%\text{CD}_3\text{CN}$), -11.1 , -15.1 , -21.1 , -34.6 , -37.2 ppm; $^1\text{H-NMR}$ (CD_3CN), 7.74 - 7.28 (m, phenyl H), 2.35 (s, $9\text{S}3 \text{ CH}_2$), 1.14 (s, carboranyl CH).

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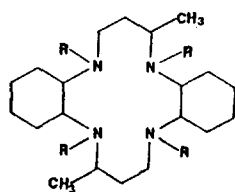
A New 14-Membered Tetraaza Macrocycle Having High Selectivity for Cu(II) Complex Formation

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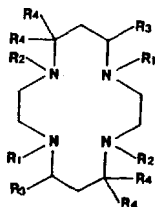
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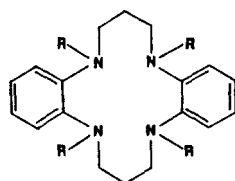
Since selective separation and transport of metal ions are important subjects in the field of waste treatment, hydrometallurgy, or biochemistry, many efforts have been made to design ligands which show selectivity for a particular metal ion in the complex formation.^{1,2} It has been widely known that crown ethers exhibit some size-based selectivity toward alkali or alkaline earth metal ions.¹ Although most polyaza macrocyclic ligands form complexes with transition metal ions without showing considerable selectivity for the metal ions, some recent reports show that the selectivity of such ligands can be increased by their structural modification.³⁻¹⁰ For example, the 14-membered tetraaza macrocycle D containing four N-methyl groups shows higher selectivity for complex formation with Cu(II) over Ni(II) ion than the unmethylated macrocycle C.^{8,9} However, the selectivity of most polyaza macrocyclic ligands studied so far is kinetical rather than thermodynamical one and thus not very satisfactory. Therefore, we have been interested in the synthesis of highly selective macrocyclic ligands. We obtained a new per-N-methylated macrocyclic ligand 2,3,6,13,14,17-hexamethyl-2,6,13,



A: R = Me
B: R = H



C: R₁ = R₂ = R₃ = R₄ = H
D: R₁ = R₂ = Me; R₃ = R₄ = H
E: R₁ = R₂ = H; R₃ = R₄ = Me
F: R₁ = R₂ = R₃ = R₄ = Me
G: R₁ = R₃ = Me; R₂ = Et; R₄ = H



H: R = Me

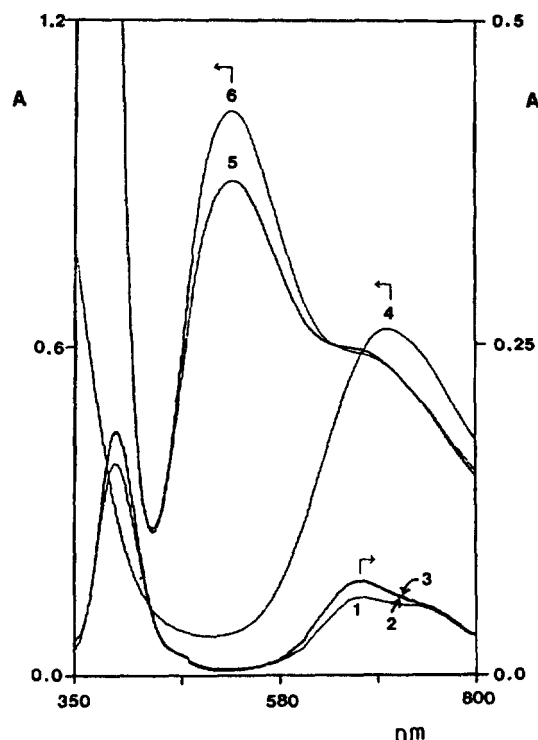


Figure 1. Electronic spectra of methanol solutions of Ni(II) acetate (1), mixture of Ni(II) acetate and A (7.5×10^{-3} M) at room temperature (2), the mixture (2) after heating at 45°C for 6 h (3), Cu(II) acetate (4), mixture of Cu(II) acetate and A (1.5×10^{-3} M) at room temperature (5), and this mixture after heating at 45°C for 6 h (6). $[\text{Ni}^{2+}] = 1.5 \times 10^{-2}$ M. $[\text{Cu}^{2+}] = 3.0 \times 10^{-3}$ M.

17-tetraazatricyclo[16,4,0^{1,18},0^{7,12}]docosane(A) that shows extraordinary high selectivity for complex formation with Cu(II) over Ni(II) ion.

New macrocycle A was obtained by the following procedure. A mixture of B (2.0 g)⁹, 85% formic acid (7.3 ml), 35% formaldehyde (7.3 ml), and distilled water (2 ml) was heated at reflux for 26 h and then cooled to *ca.* 5°C . A solution of NaOH (30 g) in water (100 ml) was added to make the pH of the solution higher than 12 and the resulting solution was extracted with chloroform. Chloroform of the extract was removed on a rotary evaporator, and a yellow oily liquid was obtained, which slowly solidified at room temperature. The product was recrystallized from 0.1 M NaOH aqueous solution-methanol mixture (Yield; $\sim 80\%$. Mass: $m/e = 392$ (M^+). $^1\text{H-NMR}$ (CDCl_3): 0.97 (d, C-Me), 2.28 (s, N-Me), 2.30 (s, N-Me). $^{13}\text{C-NMR}$: 18.8 (C-Me), 24.8, 26.2, 30.2, 33.4, 35.4 (N-Me), 35.8 (N-Me), 39.1, 49.4, 52.2, 61.3, 64.3). The infrared spectrum of A shows no peak around 3200 cm^{-1} , showing that all of the nitrogens are methylated.

The reaction of A with Cu(II) acetate in methanol followed by addition of sodium perchlorate produces red-purple crystals $[\text{Cu}(\text{A})](\text{ClO}_4)_2$ in high yield ($>90\%$).¹² The synthesis of Ni(II) complex of A by the reaction similar to that for the Cu(II) complex has also been attempted. Even after prolonged heating (>48 h) at reflux of the methanol solution of the mixture of the ligand and acetate, chloride, or nitrate salt of Ni(II) ion, the spectra of the solution was not changed. In all cases, the addition of sodium perchlorate to the re-