Synthesis and Study of Mixed Ligand-Metal Complexes of 1, 3, 7-Trimethylxanthine and 1, 3-Dimethyl-7*H*-purine-2, 6-dione with Some Other Ligands

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Abstract: This work presents synthesis and study of a new mixed ligand metal complexes of 1,3,7-trimethylxanthine and 1,3-dimethyl-7*H*-purine-2,6-dione with some other ligands like SCN and OCN ions to give the general formula $[M(Tx)_2(Tp)_2XY]$ where $M=Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$ and $Cd(II)$, $Tx=1,3,7$ -trimethylxanthine, $Tp=1,3$ -dimethyl-7*H*-purine-2,6-dione, $X=SCN$ and $Y=OCN$. The resulting products were found to be solid which have been characterized using UV-Visible and infrared spectroscopy. Elemental analyses were performed using C, H, N analysis and atomic absorption techniques. The magnetic susceptibility and the conductivity were also measured. The present results suggest that the 1,3,7-trimethylxanthine and 1,3-dimethyl-7*H*-purine-2,6-dione were coordinated with metal ions through the nitrogen atom. Thiocyanate ion was coordinated with metal ions through the sulfur atom and the cyanate ion was coordinated with metal ions through the oxygen atom.

Keywords: 1,3,7-Trimethylxanthine complexes, 1,3-Dimethyl-7*H*-purine-2,6-dione complexes,, Mixed ligand complexes, Thiocyanate complexes, Cyanate complexes.

Introduction

The purine bases (constituents of the nucleic acids) are playing an important role of biological activity. In last few years the interaction of metal ions with nucleic acids has been very active area of inorganic and structural chemistry¹. Thus, methylxanthine derivatives as possible inhibitor leads are also used therapeutically as anti-inflammatory agents, considered corrosion inhibition capability and they have significant efficiency as a non-toxic. Moreover, these derivatives are competitive inhibitors against a fungal family 18 chitinase. The enzyme

assays has also revealed that these methylxanthines are active against human chitinases²⁻⁴. The early studies indicated that the 1,3,7-trimethylxanthine ingestion could result in both increase and decrease in different individuals but more recent studies have confirmed the average increased delta activity with 1,3,7-trimethylxanthine. Thus, some studies were evaluated the possibility of the synergistic effects of the selected antibiotics with 1,3,7-trimethylxanthine against *Staphylococcus aureus*⁵.

The study of metals coordination with the purines reveals *in vitro* the mechanism of their coordination with DNA⁶. The most studies on complexes have shown that the unsubstituted purines normally coordinated to the metals via imidazole nitrogen atom⁷. In this work, the interaction of 1,3,7-trimethylxanthine and 1,3-dimethyl-7*H*-purine-2,6-dione with metal ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) is investigated.

Experimental

All chemicals were obtained from commercial sources and were used without further purifications (CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O, ZnCl₂, Cd(NO₃)₂·4H₂O, KOCN and KSCN) from Riedel–Dehaenage. 1,3,7-trimethylxanthine and 1,3-dimethyl-7*H*-purine-2,6-dione were obtained from BDH, methanol, ethanol and dimethylsulfoxide from Fluka. The I.R spectra in the range of 4000-400 cm⁻¹ were recorded as potassium bromide disc on a Shimadzu FTIR-8300 Fourier transform infrared spectrophotometer. UV-Visible spectra were measured in dimethylsulfoxide (DMSO) using Shimadzu UV-Visible recorder spectrophotometer UV-160. Elemental analysis (C, H, N) was performed by the micro analytical unit on a Berkin Elemer B-240 Elemental Analyzer. Determinations for metals were carried out using gravimetric methods. Conductivity measurements were carried out at 25 °C in DMSO using Philips Pw-9526 digital conductivity meter. Melting point was determined using a Stuart-Melting Point Apparatus. The magnetic susceptibility measurements were eventually obtained using a Balance Magnetic Susceptibility Balance Model MsB-MK1.

General procedure for synthesis

An ethanolic solution (12 mL) of 1,3,7-trimethylxanthine (Tx) (1.43-2.66 g) and an ethanolic solution (15 mL) of 1,3-dimethyl-7*H*-purine-2,6-dione (Tp) (1.23-2.70 g) respectively were added to an aqueous solution of the metal salts. This is followed by the addition of an aqueous solution (12 mL) of KOCN (0.47-0.96 g) and an aqueous solution (15 mL) of KSCN (0.87-0.57 g) respectively. After constant stirring using an appropriate amount of materials needed as decided by the molar ratio 1:2:2:1:1 (M:Tx:Tp:X:Y), the resulting precipitates were filtered off, washed several times and recrystallized with 1:3 ethanol: water mixture. Then, it was eventually dried in an oven at 65 °C.

Results and Discussion

Elemental analysis and melting point data obtained were in good agreement with the values calculated from the proposed empirical formula. The lower value observed of molar conductivities in DMSO indicates the non electrolyte behavior of the complexes⁸. Table 1 gives in details of the physical properties of the complexes.

Infrared spectra studies

Infrared spectra of free ligands

The spectrum of (Tp) shows strong bands at 3350, 1720 and 1668 cm⁻¹ that may be attributed to the $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{N}=\text{C})$ respectively. In addition, on complex formation

the band of C=N is shifted to the lower frequencies by 68-28 cm^{-1} . The spectrum of (Tx) exhibited a strong band at 1658 cm^{-1} which is attributed to the $\nu(\text{N}=\text{C})$ is also shifted to lower wave number by 58-18 cm^{-1} , all these shifted indicate that the (C=N) group is involved in complex formation. Furthermore, the spectra of the complexes exhibited weak bands between 500-545 cm^{-1} due to $\nu(\text{M}-\text{N})$. This indicates the coordination of Tx and Tp with metal ions through the nitrogen atom⁹⁻¹².

Table 1. The physical properties of the prepared complexes

Compound	Color	M. P. °C	Yield %	Elemental analysis, calc (found) %				Molar conductivity ohm^{-1}
				C	H	N	M	
[Co(Tx) ₂ (Tp) ₂ XY]	Pink	>300	70	42.341 (42.55)	3.993 (2.73)	27.772 (27.85)	6.46 (7.56)	15.62
[Ni(Tx) ₂ (Tp) ₂ XY]	Light green	>300	65	42.351 (42.56)	3.994 (4.84)	27.779 (28.81)	6.46 (6.76)	21.12
[Cu(Tx) ₂ (Tp) ₂ XY]	Gray green	>300	60	42.127 (42.14)	3.973 (3.57)	27.632 (27.79)	6.66 (7)	20.54
[Zn(Tx) ₂ (Tp) ₂ XY]	white	>300	55	42.042 (41.11)	3.965 (3.64)	27.576 (27.92)	7.13 (8.3)	18.98
[Cd(Tx) ₂ (Tp) ₂ XY]	white	>300	50	39.985 (39.93)	3.771 (3.83)	26.228 (26.43)	11.66 (12.3)	17.24

The asymmetrical and symmetrical vibrations in OCN^- were noticed at 2165 cm^{-1} and 1207 cm^{-1} respectively in the spectra of free ligand. These bands have already shifted to the higher frequencies by 35-75 cm^{-1} and 7-18 cm^{-1} respectively. Thus, the spectra of the complexes show bands in the range of 560-580 cm^{-1} which indicated that the cyanate ion was coordinated with the metal ions through the oxygen atom¹³⁻¹⁵.

The potassium thiocyanate spectrum showed a very strong band at 2048 cm^{-1} which belongs to the $\nu(\text{CN})$. This band appeared in the complexes between 2050-2140 cm^{-1} which is shifted to the higher frequencies by 2-92 cm^{-1} . Thus, the complexes exhibited weak bands between 415-440 cm^{-1} which are due to $\delta(\text{M}-\text{SCN})$. Therefore, the SCN^- was coordinated with metal ions through the sulfur atom^{14,16}. Table 2 gives the diagnostic absorptions and their assignments.

Table 2. The characteristic infrared absorptions of the prepared complexes

Compound	$\nu(\text{NH})$	$\nu(\text{OCN})_{\text{asy}}$	$\nu(\text{CN})$	$\nu(\text{C}=\text{N})$	$\nu(\text{OCN})_{\text{sy}}$	$\nu(\text{CS})$	$\delta(\text{M}-\text{OCN})$	$\nu(\text{M}-\text{N})$	$\delta(\text{M}-\text{SCN})$
[Co(Tx) ₂ (Tp) ₂ XY]	3320	2220	2060	1600	1205	730	575	500	430
[Ni(Tx) ₂ (Tp) ₂ XY]	3340	2240	2080	1640	1225	740	560	535	440
[Cu(Tx) ₂ (Tp) ₂ XY]	3340	2200	2060	1620	1225	720	565	530	415
[Zn(Tx) ₂ (Tp) ₂ XY]	3340	2220	2140	1625	1225	740	560	535	430
[Cd(Tx) ₂ (Tp) ₂ XY]	3320	2200	2050	1630	1200	730	580	545	430

Magnetic susceptibility

The magnetic moment for the complex of cobalt ion should be around 3.872 B.M while the measured value of μ_{eff} was shown to be higher than the expected value. This could be related to orbital-spin coupling¹⁷. However, the values of μ_{eff} of all Ni^{+2} and Cu^{+2} complexes were

found to be closer to that of spinning only¹⁷. The complexes of Zn^{2+} , Cd^{2+} were diamagnetic as expected from their electron configuration. The magnetic susceptibility data are presented in Table 3.

Table 3. The magnetic properties of the complexes at 25 °C

Complexes	d^n	Electron configuration	Term symbol	Ground state	μ_{eff} B.M		Orbital contribution in octahedral
					Found	Calc.	
$[\text{Co}(\text{Tx})_2(\text{Tp})_2\text{XY}]$	d^7	$t_2g^5eg^2$	4F	$^4T_{1g}$	4.258	3.872	Yes
$[\text{Ni}(\text{Tx})_2(\text{Tp})_2\text{XY}]$	d^8	$t_2g^6eg^2$	3F	$^3A_{2g}$	2.801	2.828	No
$[\text{Cu}(\text{Tx})_2(\text{Tp})_2\text{XY}]$	d^9	$t_2g^6eg^3$	2D	2E_g	1.683	1.732	No
$[\text{Zn}(\text{Tx})_2(\text{Tp})_2\text{XY}]$	d^{10}	$t_2g^6eg^4$	1S	-	diamagnetic	Zero	-
$[\text{Cd}(\text{Tx})_2(\text{Tp})_2\text{XY}]$	d^{10}	$t_2g^6eg^4$	1S	-	diamagnetic	Zero	-

Electronic spectral studies

The electronic spectra of the free ligands

The electronic spectra of the free ligand 1,3,7-trimethylxanthine (Tx) exhibited electronic transition $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ at 275, 316 and 365 nm respectively. The 1,3-dimethyl-7H-purine-2,6-dione (Tp) has shown absorption bands at 274 and 340 nm due to electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively¹⁸. The spectra of KSCN showed the electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ at 276 and 360 nm respectively. The KOCN showed absorption bands at 272 and 300 nm which belong to the electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively.

The electronic spectra of the complexes

The Co(II) complex shows electronic transitions of $^4T_{1g(F)} \rightarrow ^4A_{2g(F)}$ at 280 nm, $^4T_{1g(F)} \rightarrow ^4T_{1g(P)}$ at 429 nm and $^4T_{1g(F)} \rightarrow ^4T_{2g(F)}$ at 904 and 990 nm respectively. The electronic spectrum of Ni(II) complex exhibited absorption bands at 284 nm and 389 nm which are attributed to the electronic transitions $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$ and $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$ respectively. It is also appeared in the visible region bands at 807 and 986 nm respectively which are attributed to the electronic transition as $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$. The Cu(II) complex exhibited band in the visible region which is attributed to the electronic transition $^2E_g \rightarrow ^2T_{2g}$ which splitted into two bands as $^2b_{2g(D)} \rightarrow ^2b_{1g(D)}$ and $^2eg_{(D)} \rightarrow ^2b_{1g(D)}$ at 567 and 777 nm respectively¹⁹. Finally, Zn(II) and Cd(II) complexes with an electronic configuration of (d^{10}) did not show any (d-d) transitions. Instead the absorption bands in the spectra were due to charge transfer transitions which suffered from red and blue shift with hyper chromic effect¹⁹⁻²¹. These absorptions were fully assigned in Table 4.

Table 4. UV Visible spectra of free ligands and their complexes 10^{-3}M in DMSO

Compound	λ_{max} nm	ABS	Wave number cm^{-1}	ϵ_{max} $\text{Lmol}^{-1}\text{cm}^{-1}$	assignment
Tx	275	1.774	36363	1774	$\pi \rightarrow \pi^*$
	316	0.006	31645	6	$n \rightarrow \pi^*$
	365	0.014	27397	14	$n \rightarrow \pi^*$
Tp	274	1.728	36496	1728	$\pi \rightarrow \pi^*$
	340	0.554	29411	544	$n \rightarrow \pi^*$
KSCN	276	0.529	36231	529	$\pi \rightarrow \pi^*$
	360	0.329	27777	329	$n \rightarrow \pi^*$

Contd...

KOCN	272	0.614	36764	614	$\pi \rightarrow \pi^*$
	300	0.125	33333	125	$n \rightarrow \pi^*$
Co(Tx) ₂ (Tp) ₂ XY]	280	1.883	35714	1883	${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}(v_2)$
	429	0.017	23310	17	${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}(v_3)$
	904	0.005	11061	5	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}(v_1)$
	990	0.022	10101	22	
[Ni(Tx) ₂ (Tp) ₂ XY]	284	1.948	35211	1948	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}(v_3)$
	389	0.025	25706	25	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}(v_2)$
	807	0.003	12391	3	${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}(v_1)$
	986	0.009	10141	9	
[Cu(Tx) ₂ (Tp) ₂ XY]	290	2.192	34482	2192	(C-T)
	567	0.038	17636	38	${}^2b_{2g(D)} \rightarrow {}^2b_{1g(D)}(v_2)$
	777	0.070	12870	70	${}^2e_{g(D)} \rightarrow {}^2b_{1g(D)}(v_1)$
[Zn(Tx) ₂ (Tp) ₂ XY]	277	1.743	36101	1743	Charge transfer M→L
[Cd(Tx) ₂ (Tp) ₂ XY]	279	1.892	35842	1892	Charge transfer M→L
	321	0.014	31152	14	Red shift with hyperchromic effect
	345	0.027	28985	27	Blue shift with hyperchromic effect

Conclusion

The interaction of 1,3,7-trimethylxanthine and 1,3-dimethyl-7H-purine-2,6-dione with metal ions to yield mixed ligand complexes of $[M(Tx)_2(Tp)_2XY]$ where M= Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), Tx= 1,3,7-trimethylxanthine, Tp= 1,3-dimethyl-7H-purine-2,6-dione, X= SCN and Y= OCN was investigated. As part of our studies on the chemistry of transition metal ions and magnetic properties, we were able to investigate the paramagnetic properties of the Co(II), Ni(II) and Cu(II) complexes and the diamagnetic for Zn(II) and Cd(II) complexes. The molar conductivity of complexes in DMSO solution was non-electrolyte. However, the configuration of the complexes was confirmed that the Tx and Tp were coordinated with metal ions through the nitrogen atom, while, the metal ions were coordinated with SCN⁻ through the sulfur atom. However, the OCN was coordinated with metal ions through the oxygen atom. Therefore, it can be concluded from the presented results that the complexes have octahedral configuration, as shown in Figure 1.

Figure 1. Structure of the prepared complexes $[M(Tx)_2(Tp)_2XY]$

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References

1. Colacio R E, Lopez J D and Salas J M, *Can J Chem.*, 1983, **61**, 2506-2508.
2. Francesco V R, Ole A A, Kalpit A V, Julie A D, Daan M F and Van A, *Chem Biol.*, 2005, **12**, 973-980.
3. Paul A W, Frances M and Zoltan S, *Psychopharm.*, 1998, **136**, 264-271.
4. Thuanny F, Muriel A and Reinaldo S G, *Appl Surface Sci.*, 2006, **253**, 566-571.
5. Esimone C O, Okoye F B C, Nworu C S and Agubata C O, *Tropical J Pharm Res.*, 2008, **7**, 969-974.
6. Bojidarka I, *Turk J Chem.*, 2007, **31**, 97-103.
7. Gordon W B, Roderick J D, Keith R D and Arthur C R, *Can J Chem.*, 1983, **61**, 1132-1141.
8. Kettle S F A, *Coordination Compounds*; Thomas Nelson and Sons: London, 1975, 165.
9. Cross A D and Alan R J, *An Introduction to Partial Infrared Spectroscopy*; 3rd Ed., Butterworth: London, 1969.
10. John D R, *Application of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New Jersey, 1965.
11. William and Fleming, *Spectroscopic Methods in Organic Chemistry*; 2nd Ed., McGraw-Hill: London, New York, 1973.
12. Shayma A S and Yang F, *Am J Sci Res.*, 2009, **5**, 20-26.
13. Bailey R A and Kozak S L, *J Inorg Nucl Chem.*, 1969, **31**, 689-693.
14. Kazuo N, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 5th Edn., John Wiley and sons, Inc: New York, 1997.
15. Socrates G, *Infrared Characteristic Group Frequencies*; Wiley-Interscience publication: New York, 1980.
16. Michael B and Rudolf H, *J Electron Anal Chem.*, 1995, **385**, 105-113.
17. David N, *Complexes and First Row Transition Elements*; American Elsevier, 1984.
18. Satwinder S M, Jasjest K and Gurvinder S S, *Met Based Drugs.*, 1995, **2(1)**, 13-17, doi: 10.1155/MBD.
19. Lever A B P, *Inorganic Electronic Spectroscopy*; Elsevier publishing Co. Ltd: New York, 1968.
20. Monther Y, *The Physical Methods in Inorganic Chemistry*; Baghdad University press: Iraq, 1983.
21. Russell S D, *Physical Methods in Inorganic Chemistry*; Van Nostrand Reinhold Inc: U.S, 1965, ISBN-10: 0278920667.