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Complexes with 6-amino-5-nitroso-2-thiouracil and violuric acid derivatives containing the *fac*-$Re^{I}(CO)_3$ core: Synthesis, XRD structural and photoluminescence characterization

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ABSTRACT

The *fac*-tricarbonylrhenium(I) complexes of the 6-amino-1,3-dimethyl-5-nitroso-2-thiouracil (DANTU) and violuric acid (VIO) and its mono- (MVIO) and dimethyl (DVIO) derivatives have been prepared. The complexes have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectral methods and luminescence spectroscopy. The structures of $[ReCl(CO)_3(DANTU)]$, $[Re(H_2O)(CO)_3(VIOH_{-1})]$ and $[Re(H_2O)(CO)_3(DVIOH_{-1})]$ complexes were solved from single-crystal X-ray diffraction experiments. The coordination environment around the Re(I) may be described as a distorted octahedron in which the ligand behaves in a bidentate fashion through the nitrogen atom of the nitroso group and an adjacent carbonylic oxygen, making a five-membered chelate ring. The coordination sphere is completed with three carbonyl groups in *fac*-arrangement and one chlorine atom (DANTU complex) or water molecule (VIO complexes). The higher acidity of violuric acids, if compared with DANTU one, may explain both synergic deprotonation and chloride substitution in the $[ReCl(CO)_3]^+$ moiety to form the Re-violurato complexes.

1. Introduction

The continuing interest in the use of the radionuclide ^{99m}Tc in diagnostic nuclear medicine and the use of ^{186}Re and ^{188}Re in radiotherapy has led to the development of new radiopharmaceuticals [1,2]. The chemistry of technetium and rhenium has been well documented showing a great diversity. The *fac*-$M(CO)_3$ (M = Tc, Re) moiety recurs in many complexes having real or potential utility in medical imaging. Depending on the ligand, when bound to the *fac*-$[Re(CO)_3]$ core, the complexes act as luminescence probes; when bound to *fac*-$[^{99m}Tc(CO)_3]$ as potential radioimaging agents [3–5].

The $[M(CO)_3]^+$ core is an interesting low-spin d^6 M(I) centre. Compounds containing metals with closed-shell d^6 exhibit a different kinetic stability, charge, size and lipophilicity. These properties can be tuned with an appropriate ligand, then becoming appropriate for biomedical purposes.

Rhenium(I) tricarbonyl complexes containing bidentate heterocyclic ligands have an important application for use in solar energy conversion. They display intense luminescence in the visible region of spectrum and are stable to photodecomposition. The photobehaviour of such complexes may be discussed in terms of three types of excited states: (i) metal-to-ligand charge transfer (MLCT) states, (ii) ligand-to-ligand charge transfer (LLCT) states and (iii) intraligand (IL) states. The photophysics and photochemistry of a great variety of diimine rhenium(I) tricarbonyl complexes have been described [6–10]. They exhibit exceptionally diverse photophysical properties which occur through their lowest triplet excited states, due to rapid vibrational relaxation and intersystem crossing from the upper vibrational energy levels. This ability made these compounds very important as fluorochromes for cell imaging using fluorescence microscopy technique [11,12].

The interactions of metal ions with pyrimidine compounds have been extensively studied over the past years. It is known that thiopyrimidine derivatives act as potent inhibitors [13] and antimetabolites [14], and pyrimidine-2-thione shows pronounced in vitro bacteriostatic activity [15]. Likewise, 2-thiouracil is known as a basic constituent of some t-RNAs [16], and it exhibits antitumor and antithyroid activity because it readily incorporates into nucleic acids [17]. Violuric acids coordinate with a large number of metal ions [18–21] and they display analytical applications for the identification and determination of metal cations [22] being also used as antibacterial and antifungal agents [23]. Recent applications include their use as redox mediators in enzymatic treatment of organic pollutants of wastewater [24]. Violurato derivatives show, in coordination compounds, π-acceptor properties acting as strong-field ligands.

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In a previous paper, we described the synthesis and characterization of rhenium(I) complexes with some 5-nitrosopyrimidines [25]. Our interest in new ligand combinations with the tricarbonyl *fac*-$[M(CO)_3]^+$ core for potential applications has led us to investigate its interaction with violuric acids and one thiouracil derivative.

2. Experimental

2.1. Instrumentation

C, H, N microanalyses were performed on a Thermofinnigan Flash 1112 Series elemental analyzer. Conductivity measurements have been carried out using 10^{-3} M freshly prepared DMF solutions on a Hanna HI8820 instrument. IR spectra were measured on Bruker FT-IR Tensor-27 (4000–400 cm^{-1}, KBr pellets) and Vector-22 (600–220 cm^{-1}, polyethylene pellets) spectrophotometers. ^1H and ^{13}C NMR spectra were recorded using a Bruker DPX-300 apparatus (DMSO-d_6 solutions). Fluorescence excitation and emission spectra were measured with a Cary Elipse fluorescence spectrophotometer in CH_3CN at room temperature.

2.2. Crystallography

The measurements were performed on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The temperature (120 K) was controlled employing an Oxford Cryosystem low-temperature device. Lorentz, polarization, and multiscan absorption corrections were applied with SADABS [26]. The structure was solved by the direct method and subsequently completed by the difference Fourier recycling [27,28]. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique and the hydrogen atoms of the ligands were introduced at calculated ideal positions following riding models. In the complex $[Re(H_2O)(CO)_3(VIOH_{-1})]$, the poor data quality has limited the accuracy of the refinement. After anisotropic refinement, two main unassigned electron density peaks were observed in the final difference Fourier map, the highest being 9.2 e Å^3 at 1.25 Å from hydrogen atom H1 and the lowest being −2.40 e Å^3 at 0.82 Å from Re; despite this fact and the presence of disordered solvent molecules, the main moiety was unambiguously determined. Other experimental details for the crystallographic study are given in Table 1.

Table 1
Crystal data and structure refinement for complexes $[ReCl(CO)_3(DANTU)]\cdot 1/2CH_3CN$ (**1**), $[Re(H_2O)(CO)_3(VIOH_{-1})]\cdot 1/2H_2O$ (**2**) and $[Re(H_2O)(CO)_3(DVIOH_{-1})]$ (**4**).

	1	2	4
Empirical formula	$C_{10}H_8C_6N_{4.5}O_5ReS$	$C_7H_2N_3O_{8.5}Re$	$C_9H_8N_3O_8Re$
Formula weight	524.92	450.33	470.37
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	22.410(2)	6.345(4)	6.258(1)
b (Å)	10.954(1)	8.881(1)	8.500(1)
c (Å)	12.970(1)	10.383(9)	11.785(2)
α (°)	90	98.16(1)	83.37(2)
β (°)	100.00(1)	91.83(1)	88.53(2)
γ (°)	90	99.46(1)	77.14(1)
Volume (Å^3)	3135.5(4)	570.4(1)	607.1(2)
Z	8	2	2
D_{calc} (g cm^{-3})	2.224	2.622	2.573
μ (mm^{-1})	8.083	10.701	10.057
$F(0\,0\,0)$	1980	416	440
θ (°)	5.04–27.50	3.91–27.49	2.86–27.50
Limiting indices	$-29 \leqslant h \leqslant 29$	$-8 \leqslant h \leqslant 8$	$-8 \leqslant h \leqslant 8$
	$-12 \leqslant k \leqslant 14$	$-11 \leqslant k \leqslant 11$	$-11 \leqslant k \leqslant 11$
	$-16 \leqslant l \leqslant 16$	$-13 \leqslant l \leqslant 13$	$-15 \leqslant l \leqslant 15$
Data/restrains/ parameters	14375/0/3574	2611/0/172	2786/0/190
Goodness-of-fit on F^2	1.058	1.078	1.108
R_1/wR_2 [$I > 2\sigma(I)$]	0.0364/0.0642	0.0451/ 0.1152	0.0330/ 0.0819
R_1/wR_2 (all data)	0.0693/0.0754	0.0513/ 0.1207	0.0379/ 0.0842

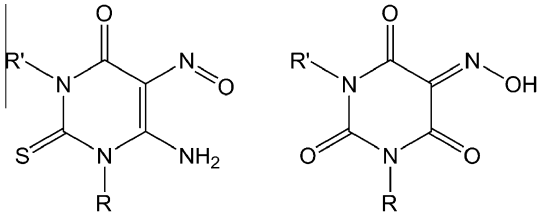

Fig. 1. More stable tautomeric structure and nomenclature of the ligands: (left) R=R′=CH_3, 6-amino-1,3-dimethyl-5-nitroso-2-thiouracil (DANTU, 6-amino-1,3-dimethyl-5-nitroso-2-thioxo-2,3-dihydropyrimidin-4(1H)-one) (right) R=R′=H, violuric acid (VIO, 5-hydroxyimino-pyrimidine-2,4,6(1H,3H,5H)-trione); R or R′=CH_3, methylvioluric acid (MVIO, 5-hydroxyimino-1-methylpyrimidine-2,4,6(1H,3H,5H)-trione); R=R′=CH_3, dimethylvioluric acid (DVIO, 5-hydroxyimino-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione).

2.3. Ligands

Commercial grade chemicals were used without further purification. The compound 6-amino-1,3-dimethyl-5-nitroso-2-thiouracil (DANTU) was synthesized by cyclocondensation of N,N′-dimethylthiourea and cyanacetic acid in acetic anhydride, followed by the nitrosation with $NaNO_2$ and acetic acid. Violuric acid derivatives were obtained by means of acid hydrolysis with HCl from the corresponding 6-amino-5-nitrosopyrimidines. Analytical and characterizational data are in agreement with the structures depicted in Fig. 1. NMR assignments were corroborated from ^1H, ^{13}C, DEPT, HMQC and HMBC (^{13}C–^1H) spectra. Data are as follows: DANTU·H_2O: IR (cm^{-1}): 3146br ν(N–H); 1692s ν(C=O); 1638m ν(C=C); 1499m ν(N=O); 1030w δ(N–H); 879m ν(C=S); 802,761w $\omega(NH_2)$. ^1H NMR (δ, ppm): 3.72 ($N1–CH_3$), 3.70 ($N3–CH_3$), 9.11, 12.85 ($C6–NH_2$); ^{13}C NMR (δ, ppm): 35.43 (C1), 36.18 (C3), 178.53 (C2), 158.35 (C4), 140.12 (C5), 144.01 (C6). VIO·H_2O: IR (cm^{-1}): 3110br ν(N–H); 1753sh, 1721s ν(C=O); 1638m ν(C=C); 1060s ν(N–O). ^1H NMR (δ, ppm): 11.39 (N1–H), 11.29 (N3–H), 14.72 (C5–N5OH); ^{13}C NMR (δ, ppm): 140.12 (C5), 149.76 (C2), 158.35 (C4), 144.01 (C6). MVIO: IR (cm^{-1}): 3114b ν(N–H); 1742m, 1665s ν(C=O); 1583m ν(C=C); 1073s ν(N–O). ^1H NMR (δ, ppm): 3.05, 3.11 ($N–CH_3$), 11.51, 11.61 (N–H), 14.71 (C5–N5OH); ^{13}C NMR (δ, ppm): 26.71, 27.36 ($N–CH_3$), 135.66, 136.22 (C5), 150.04 (C2), 158.18, 159.05 (C4), 153.78, 154.52 (C6). DVIO·H_2O: IR (cm^{-1}): 1748m, 1676b ν(C=O); 1632sh ν(C=C); 937m ν(N–O). ^1H NMR (δ, ppm): 3.11 ($N1–CH_3$), 3.17 ($N3–CH_3$), 14.78 (C5–N5OH); ^{13}C NMR (δ, ppm): 27.52 (C1), 28.21 (C3), 135.66 (C5), 150.62 (C2), 153.54 (C6), 158.19 (C4).

2.4. Preparation of the complexes

$[ReCl(CO)_3(DANTU)]\cdot 1/2CH_3CN$ (**1**): A suspension of the ligand (0.25 mmol) in acetonitrile (30 ml) was reacted with the $[ReCl(CO)_5]$ compound (0.25 mmol). The mixture was stirred and heated for three hours. Then, it was left to cool at room temperature and red crystals suitable for X-ray diffraction were obtained. $ReCl(CO)_3(DANTU)\cdot 1/2CH_3CN$: Yield *ca.* 70%; IR ($cm^{-1}$): 3203b ν(N–H); 2039s, 1939s, 1892s ν(C≡O); 1636s ν(C=O); 1596m ν(C=C); 1518m ν(N=O); 1041m δ(N–H); 879m ν(C=S); 782w, 720w $\omega(NH_2)$; 451w ν(Re–C); 273w ν(Re–Cl). ^1H NMR data (δ, ppm): 3.80 ($N1–CH_3$), 3.78 ($N3–CH_3$), 11.18, 12.18 ($C6–NH_2$);

^{13}C NMR (δ, ppm): 36.15 (C1), 37.91 (C3), 137.77 (C5), 148.11 (C6), 170.12 (C4), 176.12 (C2), 198.15, 195.31, 188.88 (CO).

[$Re(H_2O)(CO)_3(VIOH_{-1})$]·1/2$H_2O$ (**2**) and $Re(H_2O)(CO)_3$(MVIOH$_{-1}$)·1/2H_2O (**3**): The synthesis of the complexes were carried out by reacting 0.25 mmol of the ligand with 0.25 mmol of [$ReCl(CO)_5$] in methanol. A solution of the reaction product was obtained after heating at 50–60 °C and stirring for *ca.* 3 h. After this time, it was added hexane appearing a red precipitate. The solids were filtered, washed with EtOH and Et_2O and air dried. Recrystallization using acetone:H_2O (1:1) afforded crystals suitable for X-ray diffraction of compound **2** (but not very good). [$Re(H_2O)(CO)_3(VIOH_{-1})$]·1/2$H_2O$: Yield *ca.* 60%; IR (cm^{-1}): 3424b ν(O–H); 3169w ν(N–H); 2047s, 1946s, 1919s ν(C≡O); 1742m, 1725m, 1660m ν(C=O); 1494m ν(N=O); 437w ν(Re–C). ^{1}H NMR data (δ, ppm): 12.44 (N1–H), 11.09 (N3–H); ^{13}C NMR (δ, ppm): 142.88 (C5), 148.72 (C2), 153.08 (C6), 178.28 (C4), 197.58, 195.03, 192.00 (CO). [$Re(H_2O)(CO)_3(MVIOH_{-1})$]·1/2$H_2O$: Yield *ca.* 70%; IR (cm^{-1}): 3385b ν(O–H); 3208sh ν(N–H); 2044s, 1927s, 1905s ν(C≡O); 1721s, 1668m ν(C=O); 1629m ν(C=C); 1505m ν(N=O); 447w ν(Re–C). ^{1}H NMR data (δ, ppm): 3.29, 3.31 (N–CH_3), 11.36, 12.69 (N–H); ^{13}C NMR (δ, ppm): 26.30, 27.75 (N–CH_3), 142.54, 143.27 (C5), 148.88 (C2), 151.94, 152.75 (C6), 176.82, 177.43 (C4), 197.58, 194.93, 191.95 (CO).

[$Re(H_2O)(CO)_3(DVIOH_{-1})$] (**4**): To a stirred solution of DVIO (0.25 mmol) in a H_2O:acetone (1:1) mixture was added [$ReCl(CO)_5$] (0.25 mmol). The solution was heated for three hours and left to cool. Some days later, X-ray-quality red crystals were obtained. [$Re(H_2O)(CO)_3(DVIOH_{-1})$]: Yield *ca.* 60%; IR (cm^{-1}): 3447b ν(O–H)$^+$ ν(N–H); 2038s, 1944s, 1904s ν(C≡O); 1721m, 1709m, 1654m ν(C=O); 1573 ν(C=C); 1508m ν(N=O); 449w ν(Re–C). ^{1}H NMR (δ, ppm): 3.10 (N1–CH_3), 3.37 (N3–CH_3); ^{13}C NMR (δ, ppm): 27.19 (C1), 28.82 (C3), 142.87 (C5), 149.39 (C6), 151.77 (C2), 176.19 (C4), 197.51, 194.85, 191.87 (CO).

3. Results and discussion

3.1. Crystallographic studies

The molecular unit of [$ReCl(CO)_3$(DANTU)] (**1**) is depicted in Fig. 2; the XRD structures of [$Re(H_2O)(CO)_3(VIOH_{-1})$] (**2**) and [$Re(H_2O)(CO)_3(DVIOH_{-1})$] (**4**) are similar but the 6-amino group (N6) and the Cl atom are substituted by an 6-oxo group (O6) and a water molecule (Ow), respectively. Selected interatomic distances and angles useful to describe the metal coordination sphere as well as the tautomeric form (keto-oxime, keto-nitroso or nitroso-enol) of the ligands are included in Table 2. The coordination geometry at the rhenium(I) centre is distorted octahedral, with the three carbonyl groups arranged in a *facial* fashion. The *bite*

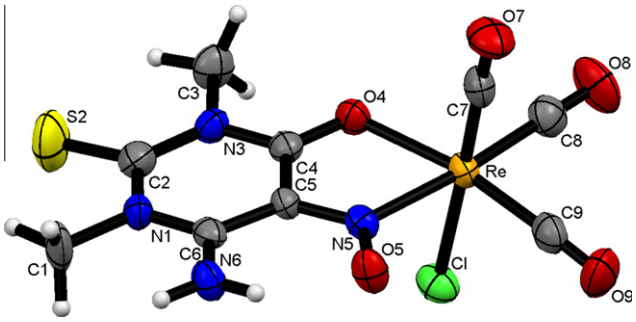

Fig. 2. ORTEP drawing (50% probability ellipsoids) and atom-labelling scheme for [$ReCl(CO)_3$(DANTU)]. The reported XRD structures of [$Re(H_2O)(CO)_3(VIOH_{-1})$] (**2**) and [$Re(H_2O)(CO)_3(DVIOH_{-1})$] (**4**) are similar but the 6-amino group (N6) and the Cl atom are substituted by an 6-oxo group (O6) and a water molecule (Ow), respectively.

Table 2
Bond lengths (Å) and angles (°) around the rhenium atom for complexes [$ReCl(CO)_3$(DANTU)] (**1**), [$Re(H_2O)(CO)_3(VIOH_{-1})$] (**2**) and [$Re(H_2O)(CO)_3(DVIOH_{-1})$] (**4**).

	1	**2**	**4**
	(X=Cl; Y=N; Z=S)	(X=Ow; Y=O; Z=O)	(X=Ow; Y=O; Z=O)
Re–C(9)	1.901(8)	1.91(1)	1.884(7)
Re–C(8)	1.948(8)	1.956(9)	1.931(7)
Re–C(7)	1.899(7)	1.914(9)	1.890(7)
Re–N(5)	2.132(5)	2.153(7)	2.130(5)
Re–O(4)	2.166(4)	2.159(6)	2.141(4)
Re–X	2.471(2)	2.202(6)	2.199(5)
C(2)–Z(2)	1.627(7)	1.23(1)	1.215(8)
O(4)–C(4)	1.256(7)	1.26(1)	1.253(8)
N(5)–C(5)	1.345(7)	1.34(1)	1.352(8)
N(5)–O(5)	1.267(6)	1.26(1)	1.248(7)
C(6)–Y(6)	1.295(7)	1.22(1)	1.219(8)
C(9)–Re–C(7)	88.6(3)	88.0(4)	88.6(3)
C(9)–Re–C(8)	88.8(3)	89.9(4)	88.1(3)
C(7)–Re–C(8)	89.1(3)	86.6(4)	88.5(3)
C(9)–Re–N(5)	97.2(2)	96.2(4)	94.6(2)
C(7)–Re–N(5)	91.7(2)	95.8(3)	95.0(2)
C(8)–Re–N(5)	174.0(2)	173.5(3)	175.6(2)
C(9)–Re–O(4)	170.5(2)	170.8(3)	170.1(2)
C(7)–Re–O(4)	96.8(2)	95.5(3)	94.2(2)
C(8)–Re–O(4)	99.1(2)	98.7(3)	101.4(2)
N(5)–Re–O(4)	74.9(2)	75.1(3)	75.7(2)
C(9)–Re–X	91.0(2)	94.4(3)	97.1(2)
C(7)–Re–X	176.7(2)	177.5(3)	173.3(2)
C(8)–Re–X	94.2(2)	93.3(3)	95.2(2)
N(5)–Re–X	85.1(1)	84.0(2)	81.2(2)
O(4)–Re–X	83.2(1)	82.1(2)	79.5(2)

angle formed by O4–Re–N5 is significantly narrowed from the expected octahedral 90° value to 74.9° (**1**), 75.1° (**2**) and 75.7° (**4**), respectively. This value is consistent with those obtained for other tricarbonyl rhenium(I) compounds with -diimine, lumazines and hydrazones ligands that form five-membered metallocyclic rings [29–32].

The Re–carbonyl bond distances (1.886–1.957 Å) are consistent with those found in other Re–tricarbonyl complexes and show multiple-bond character as consequence of the π-acceptor ability of the CO. The C–Re–C angles have an average value of 89.5°. Also, the distances Re–N5, Re–O4, Re–Cl and Re–Ow are longer than those expected due to the *trans* influence of the carbon monoxide ligands. As it is previously reported [25], in every structure, the carbon monoxide in *trans* with the N5 atom seems to be weaker bound to the Re, since the Re–C8 distances are always 0.04–0.05 Å longer than Re–C7 and Re–C9 ones, a concomitant shortening by *ca.* 0.02 Å of C8–O8 bonds taking place.

In complex **1**, the ligand DANTU is almost planar with small deviations from the mean plane. The angle between the ligand and the chelate ring (Re–O4–C4–C5–N5) is 5.5(3)°. The geometrical data suggest a significant electronic delocalization and the presence of the ligand in its more stable ketone-nitroso tautomeric form [33], as it has been previously reported for [$ReCl(CO)_3$(DANU)]·CH_3CN [25]. Although the sulphur atom displays important coordinative properties, its involvement is hindered at all by the presence of methyl-blocked pyrimidine nitrogens, since usually it needs an available adjacent deprotonated nitrogen atom to make a four-membered chelate ring [34].

Despite violuric acid ligands contain one acidic proton involved in a ketoneoxime⇆nitrosoenol tautomeric equilibrium, XRD experiments clearly confirmed the existence of the metal-free tautomeric ketone-oxime form [35]. However, crystallographic data suggest the coordination to the rhenium(I) centre favours the ligand deprotonation and the change to the nitrosoenolato form. Thus, the N5–O5 and C5–N5 distances are shorter and longer than those found in the free ligand (0.092 Å and 0.052 Å, respectively),

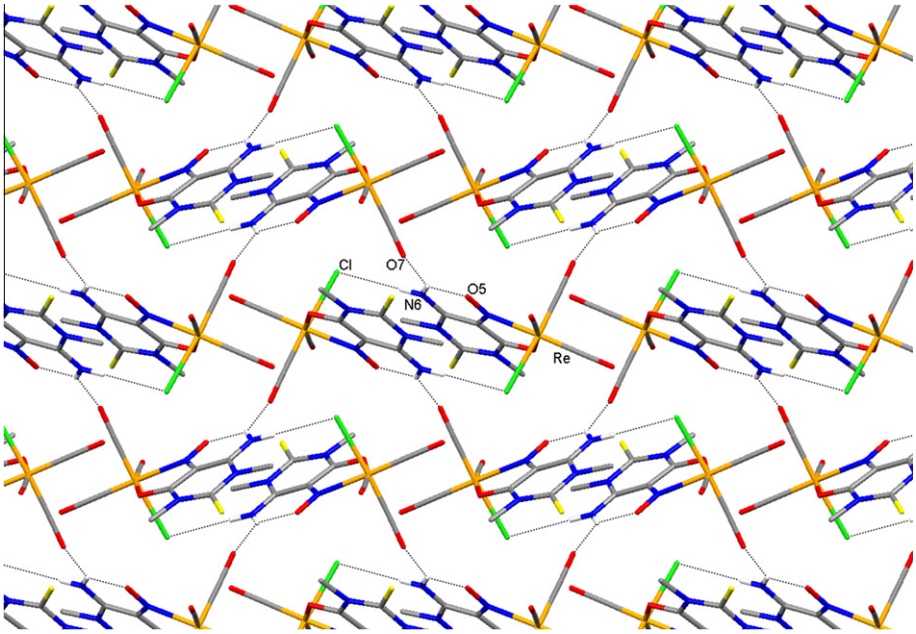

Fig. 3. View, down the *a* axis, of the 2D-hydrogen bonded network in the $[ReCl(CO)_3(DANTU)]\cdot 1/2CH_3CN$ structure. Disordered acetonitrile molecules are omitted for clarity. H-bonds parameters (D···A (Å); <D–H···A (°)): N6–H···O5, 2.604(6), 130; N6–H···O7 (x, $-y$, $1/2 + z$), 3.024(7), 142; N6–H···Cl ($1/2 - x$, $1/2 + y$, $1/2 - z$), 3.306(5), 148.

this fact strongly supporting the presence of a 5-nitroso group (–N=O) over a 5-oxime one (=N–O). The C2–O2 and C6–O6 distances correspond to a double bond (*ca.* 1.22 Å) whereas C4–O4 distance is longer (*ca.* 1.25 Å) as consequence of both deprotonation and coordination effects. A similar behaviour of the Re-coordinated $DVIOH_{-1}$ anion has been found, in a similar way than the analogous $VIOH_{-1}$ complex and other related coordination compounds [18]. The remaining distances and angles are similar to those of violuric acid. Also, the higher acidity of violuric acids, if compared with DANTU one, promotes both the deprotonation of violuric acids to bind to Re(I) and the substitution of the chloride ligand by water in the tricarbonyl-Re-core.

In every complex, the organic moiety and the five-membered chelate ring are *quasi*-coplanar because the pyrimidine skeleton least-squares plane and the chelate rings (Re–O4–C4–C5–N5) define acute angles of 1.5(4)° (**2**) and 2.2(3)° (**4**). The pyrimidine cycles show small deviations from planarity: N1 (0.011(7) Å) for Re/VIO and C2 (0.024(7) Å) and N3 (−0.022(6) Å) for Re/DVIO.

In the crystal structure of $[ReCl(CO)_3(DANTU)]\cdot 1/2CH_3CN$, the hydrogen bonding network is formed by sheets which are placed parallel to the *bc* plane, as shown in Fig. 3. In the $[Re(H_2O)(CO)_3(DVIOH_{-1})]$ structure, a 2D supramolecular layer parallel to the *ab* plane is formed by means of the cooperative effect of O(carbonyl)···O(carbonyl) van der Waals interactions with three hydrogen bonds involving the coordinated water molecules (see Fig. 4).

3.2. Conductivity and spectral studies

The molar conductivity measurements indicate all rhenium(I) compounds behave as non-electrolyte [36].

In the infrared spectra of metal complexes, tentative assignments for the more significant bands have been made by comparison with the ligands ones [37]. The spectra of the complexes exhibit a sharp, strong band over 2040 cm^{-1} and two broad bands around 1940 and 1900 cm^{-1} attributed to ν(C≡O) of the *fac*-$[Re(CO)_3]^+$ unit.

The spectrum of complex **1** exhibits one broad band around 3200 cm^{-1} corresponding to the antisymmetric stretching vibration of 6-amino group which clearly supports the presence of the thiopyrimidine ligand in ketone-nitroso form. The ligand bands are slightly displaced to a upper wavenumber by coordination. The shift to a lower wavenumber of the ν(N=O) vibration (*ca.* 20 cm^{-1}) strongly suggests, in accordance with X-ray structural results, the coordination through the N5 nitrogen.

The infrared spectra of **2**, **3** and **4** show as main feature the disappearance of ν(N–O) band (*ca.* 930–1080 cm^{-1}) from the oxime group and the concomitant appearance of the ν(N=O) band (*ca.* 1490–1510 cm^{-1}) from the nitroso group indicating that, upon complexation, the ketone-oxime form of the free-ligands becomes completely in the nitroso-enolato one; also, the bands assignable to C–O stretching vibrations are also shifted [18–20] due to both deprotonation and coordination cooperative effects.

In the 600–200 cm^{-1} range, one band, at around 451 cm^{-1} including the stretching vibrations of Re–C and Re–O, and another, at around 270 cm^{-1}, due to ν(Re–Cl) [38] for complex **1**, can be observed.

The coordination mode of the ligands in the rhenium(I) complexes deduced from IR data is confirmed by a general deshielding of some signals in NMR. In the ^{1}H NMR spectra of the complexes the signals are downfield shifted due to the coordination process. The ligand DANTU forms a strong intramolecular H-bond between the oxygen atom from the 5-nitroso group and one hydrogen atom from the 6-amino group. This explains the appearance of two signals in ^{1}H NMR spectra at around 12 and 11 ppm, the proton involved in the H-bond being downfield shifted.

As it was before mentioned, the violurato ligands in the rhenium(I) complexes are found in the nitroso-enolato tautomeric form. Due to the *pseudo*-symmetry of the uracil moiety through the *pseudo*-two-fold axis connecting O2–C2–C5–N5 atoms, the free-MVIO could establish an intramolecular H-bond through either =N–OH···O4 or =N–OH···O6, an identical duality for the coordination (N5,O4 or N5,O6) can take place as well. Both reasons can explain the couple of signals assignable to both the N–CH_3 and N–H groups in the ^{1}H NMR spectra of free-MVIO and the Re-MVIO compounds; accordingly, the ^{13}C NMR spectra of free-MVIO and Re-MVIO display two signals for methyl, C4, C5 and C6 carbon atoms due to the existence of two potential *quasi*-equivalent metal-binding arrangements, thus each carbon atom lying into two slightly different electronic surroundings.

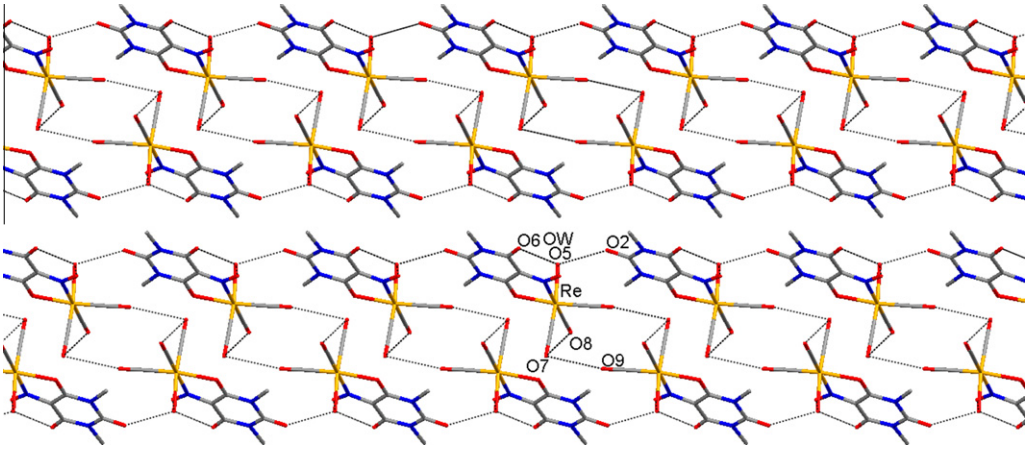

Fig. 4. Crystal packing diagram of $[Re(H_2O)(CO)_3(DVIOH_{-1})]$ from the *a* direction showing the arrangement of the bidimensional H-bonded sheets. H-bond parameters (D···A (Å)): Ow···O2 (x, $1-y$, z), 2.651; Ow···O5 ($1-x$, y, z), 2.796; Ow···O6 ($1-x$, y, z), 2.758. O···O van der Waals' interactions (Å): O8···O7 ($-1+x$, y, z) 2.993; O9···O7 ($1-x$, $-y$, $-z$) 3.021.

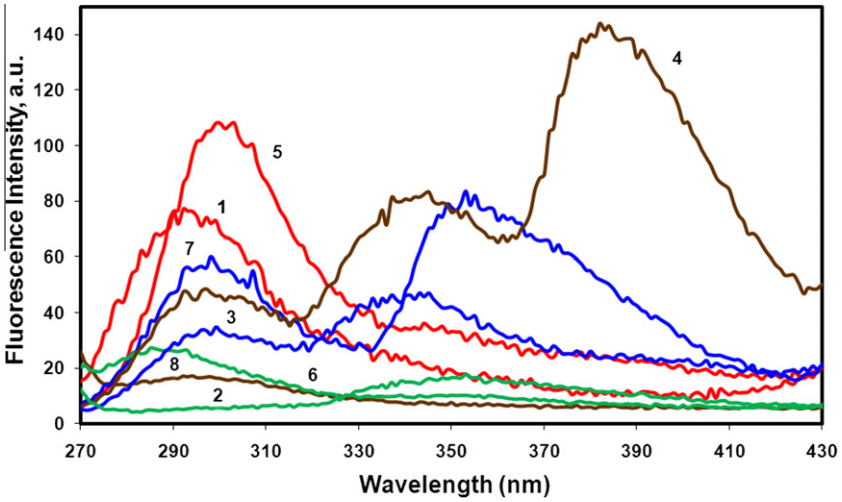

Fig. 5. Emission spectra of DANTU (**1**), VIO (**2**), MVIO (**3**), DVIO (**4**), $[ReCl(CO)_3(DANTU)]\cdot 1/2CH_3CN$ (**5**), $[Re(H_2O)(CO)_3(VIOH_{-1})]\cdot 1/2H_2O$ (**6**), $Re(H_2O)(CO)_3(MVIOH_{-1})\cdot 1/2H_2O$ (**7**), $[Re(H_2O)(CO)_3(DVIOH_{-1})]$ (**8**).

On comparing the ^{13}C NMR spectra of complexes with those of free ligands, a downfield shift of the signal of the C4 atom (~12–18 ppm) can be observed. The tricarbonylrhenium(I) core has a dual function as σ acceptor and π donor but, in our case, we can conclude that donor character of O4 atom predominates over the π-backbonding of Re(I) to the exocyclic carbonyl group. The signal of the carbon C5 is upfield shifted (~3 ppm) in Re(I)–DANTU complex because of the electronic effects in the heterocyclic ring, whereas in the rhenium(I) complexes of violuric acids this signal is deshielded around 8 ppm, as consequence of the different tautomeric form present.

3.3. Luminescent properties

The photochemistry of diimine rhenium(I) tricarbonyl complexes has been extensively studied and they play and important role in understanding the photophysical and light-induced electron-transfer and electronic energy-transfer processes [7–10,31].

Fig. 5 displays the emission data of the complexes in CH_3CN solution at room temperature (10^{-5} M). The emission spectrum of DANTU and Re/DANTU complex were measured from 250 nm to 450 nm with an excitation wavelength of 226 nm. The free ligand shows a luminescence band at 290 nm assigned to a $\pi-\pi^*$ transition. In the rhenium(I) complex, a shift to a lower energy is observed (10 nm) with increase of the fluorescence intensity. Also, it can be observed a shoulder over 360 nm which is assigned to a metal-to-ligand charge-transfer (MLCT) $d\pi(Re)-\pi^*$ (ligand) transition.

A weak emission is observed for VIO and Re–VIO complex when excited to 225 nm. The ligand VIO shows a band around 350 nm ($\pi-\pi^*$ transition) which is blue-shifted in the rhenium(I) complex (65 nm).

The emission spectrum recorded at 225 nm for MVIO shows two bands at 294 and 350 nm which are assigned to $\pi-\pi^*$ transitions. In the Re/MVIO complex, the band to 350 nm is displaced to 325 nm as consequence of the coordination of the ligand to the metal ion. The absence of emission for complex **4** at 242 nm, suggests that the complex formation quenches the $\pi-\pi^*$ emission of the ligand DVIO.

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Appendix A. Supplementary material

CCDC 775743, 775744 and 775745 contains the supplementary crystallographic data for compounds **1**, **2** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.11.009.

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