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Phenylimido Complexes of Technetium and Rhenium with Maleonitriledithiolate

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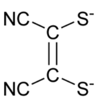
Abstract. $[Tc(NPh)Cl_3(PPh_3)_2]$ or $[Re(NPh)Cl_3(PPh_3)_2]$ react with two equivalents of Na_2mnt (mnt^{2-} = 1,2-dicyanoethene-1,2-dithiolate) with formation of anionic complexes of the composition $[M(NPh)(mnt)_2]^-$. The products can be isolated as large red blocks of their $AsPh_4^+$ salts. The complex anions contain square-pyramidal coordinated metal atoms with the phenylimido ligands in apical positions. The M–N–C bonds are almost linear. A similar phenylimido complex with an additional amino group was synthesized from $[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$. The presence of such substituents may allow coupling of the metal complexes to biomolecules such as peptides, proteins, or sugars, provided the M=N bonds are sufficiently stable against hydrolysis.

Introduction

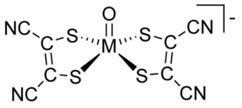
The use of ^{99m}Tc compounds in diagnostic nuclear medicine is well-established[1] and ^{186}Re and ^{188}Re are β-emitting isotopes with radiation properties, which make them interesting for therapeutic purposes.[2] For both applications, an exact knowledge of the coordination chemistry of the elements is required. Of particular interest is the stability of cores (MO^{3+}, MO_2^+, MN^{2+}, $MNPh^{3+}$), which are characteristic for technetium and rhenium complexes in higher oxidation states. Frequently, hydrolysis of the nitrogen-containing compounds and their conversion into oxido complexes is observed, which restricts their suitability as potential radiopharmaceuticals.[1–4]

Chemical studies with technetium are commonly done with the long-lived isotope ^{99}Tc, which is a weak β-emitter with a half-life of about 2×10^5 years. This isotope is available in macroscopic amounts and allows conventional chemical studies provided that some elemental rules of radiation protection are respected.

Herein, we report the synthesis and structural characterization of the first phenylimidotechnetium(V) and phenylimidorhenium(V) complexes with 1,2-dicyanoethene-1,2-dithiolate (mnt^{2-}) (**1**). Pentacoordinate technetium and rhenium complexes with this dithiolene ligand are known with the oxido (**2**) and nitrido cores (**3**).[5–7] Additionally, one technetium(IV) tris(dithiolene) complex[8] and two mixed-ligand species are known.[9,10]

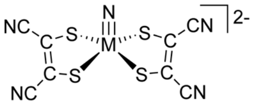


(**1**)



(**2**)

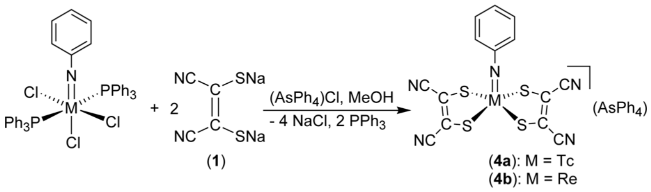
M = Tc, Re



(**3**)

Results and Discussion

Reactions of the sparingly soluble phenylimido complexes $[M(NPh)Cl_3(PPh_3)_2]$ (M = Tc and Re) with Na_2mnt in methanol give dark red solutions, from which the tetraphenylarsonium salts of the $[M(NPh)(mnt)_2]^-$ complexes could be isolated as dark red crystals (Scheme 1).



Scheme 1. Syntheses of the complexes.

The products are stable in air and readily soluble in CH_2Cl_2 or acetone. Expectedly, their IR spectra show the characteristic C≡N stretches at 2205 cm^{-1}. The M=NPh stretches appear at 1020 cm^{-1} for the technetium complex and 1030 cm^{-1} for its rhenium analogue. The ^{1}H NMR signals of the phenylimido ligands appear upfield-shifted with respect to the protons of the tetraphenylarsoniun counterion. The FAB$^-$ MS spectrum of the rhenium compound gives evidence for the molecular anion at m/z = 558.

X-ray diffraction studies on **4a** and **4b** confirm the spectroscopic results. The complex ions each contain five-coordinate metal atoms with square-pyramidal coordination spheres. Figure 1 illustrates the molecular structure of the

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$[Tc(NPh)(mnt)_2]^-$ ion. The basal plane of the square pyramid is formed by the sulfur atoms of two mnt^{2-} ligands, and the nitrogen atom of the phenylimido unit forms its apex. The structure of the $[Re(NPh)(mnt)_2]^-$ ion is virtually identical with unexceptional thermal ellipsoids. Thus, there is no extra figure for this compound. Typical bond lengths and angles of both complexes are compared in Table 1. The atomic labeling scheme of Figure 1 has also been applied for the rhenium compound.

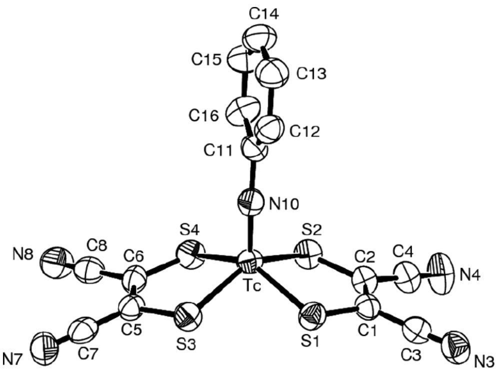


Figure 1. Ellipsoid representation[11] of the complex anion of $(AsPh_4)[Tc(NPh)(mnt)_2]$ with 50 % probability. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths /Å and angles /° in the structures of the $[M(NPh)(mnt)_2]^-$ anions (M = Tc, Re).

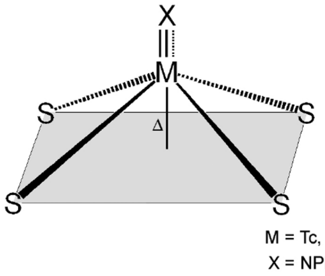
	4a	**4b**
M–N10	1.675(5)	1.706(2)
N10–C11	1.40(1)	1.396(4)
M–S1	2.335(2)	2.336(1)
M–S2	2.329(2)	2.324(1)
M–S3	2.323(2)	2.333(1)
M–S4	2.330(2)	2.324(1)
S1–C1	1.744(6)	1.746(3)
S2–C2	1.746(7)	1.747(3)
C1–C2	1.36(1)	1.356(4)
S3–C5	1.731(7)	1.746(3)
S4–C6	1.742(7)	1.747(3)
C5–C6	1.36(1)	1.349(5)
M–N10–C11	168.2(5)	169.2(2)
N10–*M*–S1	109.2(2)	108.8(1)
N10–*M*–S2	106.1(2)	106.3(1)
N10–*M*S3	107.8(2)	107.6(1)
N10–*M*–S4	104.9(2)	105.8(1)
S1–*M*–S4	145.9(1)	145.4(1)
S2–*M*–S3	146.1(1)	146.1(1)
S1–*M*–S2	85.4(1)	85.3(1)
S1–*M*–S3	84.6(1)	84.6(1)
S2–*M*–S4	84.6(1)	84.7(1)
S3–*M*–S4	85.8(1)	85.5(1)

The Tc–N and Re–N bond lengths are in the range of double bonds and the *M*–N–C angles are almost linear with values of 168.2(5) and 169.2(2)°.

The metal atoms are situated by 0.681(1) Å (technetium complex) and 0.686(1) Å (rhenium complex) above the basal plane formed by the four sulfur atoms. A similar bonding situation is found in corresponding oxido and nitrido complexes and commonly discussed as a consequence of the steric bulk of the multiply bonded ligands. With the compounds described in this paper, there exists a consistent set of pentacoordinate, anionic technetium(V) and rhenium(V) oxido, nitrido, and phenylimido complexes with each two mnt^{2-} co-ligands.

Principal structural data of the compounds are summarized in Table 2. They suggest a larger extent of steric effects in the oxido and phenylimido complexes compared with the nitrido compounds. This is indicated by the generally larger *X*–*M*–S angles and the fact that the metal atoms are more displaced from the basal planes of the square-planar complexes than in the nitrido analogue. On the other hand, a higher degree of π bonding is expected for the nitrido ligand, which is best reflected by the significantly longer *M*–S bonds.[7] The bonding parameters of the phenylimido complexes under study suggest a bonding situation between those of the oxido and the nitrido complexes. This is evident by all listed parameters in Table 2.

Table 2. Selected bonding parameters in $[M(NPh)(mnt)_2]^-$, $[MO(mnt)_2]^-$ and $[MN(mnt)_2]^{2-}$ (M = Tc and Re).



	$[M(NPh)(mnt)_2]^-$	$[MO(mnt)_2]^{-[5,6]}$	$[MN(mnt)_2]^{2-[6,7]}$
M–X /Å	Tc 1.68	Tc 1.66	Tc 1.59
	Re 1.71	Re 1.67	Re 1.65
M–S_{mean} /Å	Tc 2.329	Tc 2.315	Tc 2.391
	Re 2.329	Re 2.314	Re 2.357
X–M–S_{mean} /°	Tc 107.0	Tc 108.7	Tc 104.3
	Re 107.1	Re 108,2	Re 105.8
Δ /Å	Tc 0.68	Tc 0.74	Tc 0.59
	Re 0.69	Re 0.72	Re 0.64

The results may support (also with respect to the almost linear *M*–N–C bonds) a treatment of NPh^{2-} ligands in complexes with metals in high formal oxidation states as “nitrenes” with formal metal–nitrogen triple bonds rather than as “imides” with formal double bond character. Comprehensive discussions about the nature of various types of metal–nitrogen multiple bonds are contained in early reviews[12–15] and have been extensively reconsidered several years ago.[16] The suggested strong relationship between nitrido and imido compounds has finally also been experimentally proven by the synthesis of imido compounds starting from nitrido complexes by electrophilic attacks at the nitrido ligands. This has successfully been demonstrated with triphenylcarbenium salts[17,18] and *in situ* produced carbocations, e.g. with the electrophilic intermediates of acidic acetone condensation.[19]

It is noteworthy, that, in contrast to previous reports on imidorhenium(V) compounds,[3,4] no hydrolytic decomposition has been observed for the phenylimido complexes reported in this paper. This recommends them for considerations with respect to nuclear medical applications. Thus, we prepared an analogous complex to compound **4b**, which carries an additional amino group at the phenyl ring of the imido ligand. With this modification, coupling reactions with biorelevant molecules such as peptides are possible. An appropriate starting material, $[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$, has previously been published by *Machura* and co-workers.[20]

The reaction of $[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$ with Na_2mnt in methanol results in a rapid dissolution of the green solid and the formation of a red solution. Addition of $(AsPh_4)Cl$ results in a red solid of $(AsPh_4)[Re(NC_6H_4\text{-}4\text{-}NH_2)(mnt)_2]$ (**5**). Recrystallization from CH_2Cl_2/isopropanol gives long, red needles. The IR spectrum of the compound is similar to that of **4b** with an intense $\nu_{C\equiv N}$ vibration at 2200 cm^{-1}. Additionally, medium bands at 3450 and 3360 cm^{-1} can be assigned to the NH frequencies of the amino group.

Figure 2 shows a structural plot of the complex anion of compound **5**, which has also been studied by X-ray diffraction. The compound crystallizes in the orthorhombic space group $Pna2_1$ with a unit cell of the dimensions a = 25.881(2) Å, b = 6.492(1) Å and c = 22.589(2) Å. The obtained data set with wR_2 = 0.1062 was not of sufficient quality to justify a comprehensive discussion of the crystallographic data. The results of the study, however, unambiguously confirm the composition of the complex cation and all main structural features of compound **4b** do also apply for **5**.

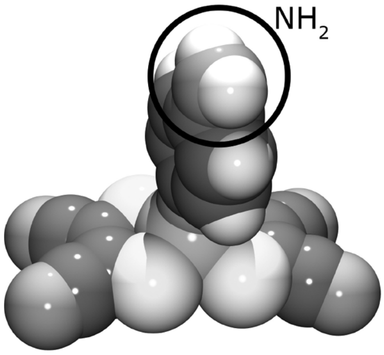


Figure 2. Space-filling representation of the complex anion of **5** with a terminal NH_2 group being far away from the coordination sphere.

The phenyl ring of the imido ligand in complex **5** acts as a spacer and, thus, the terminal NH_2 group is readily accessible for coupling reactions with activated peptides and proteins. This holds also true for phenylimido complexes with other, more bulky, chelating ligands, which might be more appropriate for biological applications than maleonitriledithiolate.

Experimental Section

Materials and Measurements

The starting complexes $[Tc(NPh)Cl_3(PPh_3)_2]$,[21] $[Re(NPh)Cl_3(PPh_3)_2]$,[22] $[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$,[20] and Na_2mnt[23] were prepared following literature procedures. The synthesis of $[Re(NPh\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$ was slightly modified to improve the yield and the purity of the product. Infrared spectra were measured as KBr pellets with a Shimadzu FT IR spectrometer between 400 and 4000 cm^{-1}. Elemental analyses were determined with a Heraeus vario EL elemental analyzer. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

Syntheses

$[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$: $[ReOCl_3(PPh_3)_2]$ (450 mg, 0.54 mmol) was suspended in acetone (15 mL). PPh_3 (2.5 g, 9.54 mmol) and 4-NH_2-aniline (100 mg, 0.92 mmol) were added in acetone (5 mL). The mixture was heated under reflux for 3 h. The resulting olive green precipitate was filtered off and washed with ethyl ether. Yield 350 mg (75 %). Elemental analysis calcd. $C_{42}H_{36}Cl_3N_2P_4Re$: C 54.7; H 3.9; N 3.0 %; found: C 54.8; H 3.9; N 2.8 %. **IR** (KBr): $\tilde{\nu}$ = 3460 (m), 3335 (st), 3195 (w), 3055 (w), 1615 (st), 1585 (st), 1480 (m), 1435 (m), 1370 (st), 1325 (m), 1190 (w), 1165 (st), 1090 (m), 1030 (w), 1005 (w), 925 (w), 845 (w), 745 (m), 695 (st), 600 (w), 565 (w), 520 (st), 515 (st), 450 (w), 425 (w) cm^{-1}.

4a: A suspension of $[Tc(NPh)Cl_3(PPh_3)_2]$ (82 mg, 0.1 mmol) and Na_2mnt (51 mg, 0.4 mmol) in methanol (15 mL) was heated under reflux for 1 hour. After cooling to room temperature, $(AsPh_4)Cl{\cdot}2H_2O$ (42 mg, 0.1 mmol) in methanol (1 mL) was added. The solvent was removed in vacuo and the resulting red-brown residue was washed with ethyl ether and recrystallized from methanol. Yield 45 mg (55 %). **IR** (KBr): $\tilde{\nu}$ = 3060 (w), 2960 (w), 2915 (w), 2205 (st), 1500 (m), 1480 (m), 1465 (m), 1440 (st), 1310 (m), 1185 (w), 1150 (m), 1110 (w), 1080 (m), 1020 (m), 995 (m), 940 (w), 900 (w), 840 (w), 740 (st), 685 (st), 505 (m), 465 (st) cm^{-1}.

4b: $[Re(NPh)Cl_3(PPh_3)_2]$ (91 mg, 0.1 mmol) was suspended in methanol (30 mL) and treated with Na_2mnt (43 mg, 0.23 mmol). After heating to reflux for 10 min, a clear red solution was obtained. $(AsPh_4)Cl{\cdot}2H_2O$ (42 mg, 0.1 mmol) was added. Deep red crystals deposited upon slow evaporation. Yield 54 mg (57 %). Elemental analysis: $C_{38}H_{25}AsN_5ReS_4$: calcd. C 48.5; H 2.7; N 7.4; S 13.6 %; found: C 48.4; H 2.4; N 7.4; S 13.6 %. **IR** (KBr): $\tilde{\nu}$ = 3060 (w), 2205 (st), 1580 (w), 1510 (st), 1475 (st), 1440 (st), 1355 (st), 1185 (w), 1155 (m), 1080 (m), 1030 (w), 995 (m), 740 (st), 685 (st), 505 (m), 465 (m) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.9–7.6 (m, 20 H, As-Ph), 7.3–6.9 ppm (m, 5 H, N-Ph). FAB$^-$-MS: m/z 558 M^-, 482 M^- - $(C\text{–}CN)_2$, 374 $[Re(NPh)S_3]^-$.

5: $[Re(NC_6H_4\text{-}4\text{-}NH_2)Cl_3(PPh_3)_2]$ (93 mg, 0.1 mmol) was suspended in methanol (50 mL) and treated with Na_2mnt (51 mg, 0.40 mmol). After heating to reflux for 10 min, a clear red solution was obtained. $(AsPh_4)Cl{\cdot}2H_2O$ (42 mg, 0.1 mmol) was added and the solvent was removed in vacuo. The residue was washed with water and ethyl ether. Recrystallization from CH_2Cl_2/isopropanol gave long, red needles. Yield 22 mg (23 %). Elemental analysis: calcd. $C_{38}H_{26}AsN_6ReS_4$: C 47.7; H 2.7; N 8.8; S 13.4 %; found: C 48.4; H 2.3; N 8.5; S 13.1 %. **IR** (KBr): $\tilde{\nu}$ = 3450 (st), 3360 (st), 3060 (w), 2270 (w), 2200 (st), 1615 (st), 1590 (st), 1505 (m), 1490 (st), 1440 (st), 1340 (w), 1290 (m), 1185 (w), 1165 (m), 1150 (m), 1115 (m), 1080 (m), 1020 (m), 995 (m), 920 (w), 820 (m), 745 (st), 685 (st), 600 (w), 505 (m), 465 (m) cm^{-1}.**^{1}H NMR** ($CDCl_3$): δ = 7.8–7.6 (m, 20 H, As–Ph), 6.6–6.4 ppm (m, 5 H, N–Ph). FAB$^-$-MS: m/z 573 M^-, 481 M^- - $(C\text{–}CN)_2$ -NH_2, 389 $[Re\{NPh(p\text{-}NH_2)\}S_3]^-$.

X-ray Crystallography

The intensities for the X-ray determinations were collected with a STOE IPDS 2T instrument with Mo-K_α radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS-97 and SHELXL-97.[24] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of SHELXL. Numerical absorption correction was applied for compound **4b**, whereas such a procedure did not improve the results of the refinement of the technetium compound with a linear absorption coefficient of just 1.559. More details on data collections and structure calculations are summarized in Table 3.

CCDC-795336 (**4a**) and CCDC-795337 (**4b**) contain the supplementary crystallographic data for the structures in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

Table 3. Crystal data and refinement results.

	4a	**4b**
Empirical formula	$C_{38}H_{25}AsN_5S_4Tc$	$C_{38}H_{25}AsN_5S_4Re$
Formula weight	852.79	940.99
Temperature /K	200(2)	200(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a /Å	12.232(2)	12.340(1)
b /Å	12.772(2)	12.733(1)
c /Å	13.035(2)	13.010(1)
α /°	64.46(1)	64.19(1)
β /°	83.23(1)	83.50(1)
γ /°	88.67(1)	89.01(1)
V /Å^3	1823.6(4)	1827.4(2)
Z	2	2
$D_{calcd.}$ /g·cm^{-3}	1.553	1.710
μ /mm^{-1}	1.559	4.487
F(000)	856	920
Absorption correction	None	Integration
T_{max}/T_{min}	–	0.5379 / 0.3496
Collected reflections	11629	19530
Unique reflections / R_{int}	6236 / 0.1004	9754 / 0.0429
Data / Parameters	6236 / 442	9754 / 442
R values [$I > 2\sigma(I)$]	R_1 = 0.0551	0.0288
	wR_2 = 0.0959	0.0590
Goodness of-fit, S	0.944	0.910

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